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## PREFACE

A review of physical chemistry should provide a critical survey of the scientific matters of interest to physical chemists. However, a demarcation line must be drawn somewhere. Thus, we stop short of a detailed treatment of nuclear theory but extend our borders far enough to include Proteins and Synthetic Polypeptides.

This year we have nineteen chapters. Although this is fewer than usual, the chapters are, in turn, somewhat longer. This does not represent a policy change but simply the occurrence of unexpected events which prevented two authors from completing their reviews. The omitted fields will be treated next year.

Stabilized Free Radicals, High Temperature Chemistry, Ion Exchange, and Physical Organic Chemistry are important fields appearing this year which are not always included.

We are fortunate to have Mrs. Anne Bogley as editorial assistant. Dr. Donald Kupke has once again compiled the subject index. The members of the Editorial Committee express their thanks for this assistance. To the authors of the chapters who have generously contributed expert judgment and many hours of hard labor, we express our deep appreciation.

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## ERRATA

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Page 198, reference 65: *for* Ferry, J. D., Child, W. C., Zand, R., Stern, D. M., Williams, M. L., and Landel, R. F., *read* Ferry, J. D.

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Page 321, line 21: *for* $OAH^2\Sigma^+$, *read* $A\ ^2\Sigma^+$

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# THERMOCHEMISTRY AND THERMODYNAMIC PROPERTIES OF SUBSTANCES[1]

By Julian M. Sturtevant[2]

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As has been the case in recent reviews in this series, limitations of space make it necessary to summarize most of the available information in brief tabular form. Even in this brief form, an arbitrary selection of material has been required and many topics of thermodynamic interest have been omitted. Although an attempt has been made in the tabular summaries to secure adequate coverage of researches leading to information on the properties of pure substances, multicomponent systems have not been completely surveyed. Studies pertaining to the thermodynamics of surfaces and adsorption processes and ion exchange have not been included. The thermodynamic properties of liquid mixtures and many aspects of the thermodynamics of liquid solutions have been omitted. Equilibrium and thermochemical data for reactions in solution have been excluded, except for equilibrium data pertaining to the formation of coordination complexes. Material reported only in *Dissertation Abstracts* has not been included.

## GENERAL

Janz (1) has published a brief textbook on the statistical and empirical estimation of thermodynamic properties. Recent developments in thermochemistry have been very well summarized by Skinner (2). Greenshields & Rossini (3) and Benson & Buss (4) have given schemes for the empirical estimation of thermodynamic properties; the latter authors have employed an interesting approach to this problem based on the redistribution reaction [cf., Skinner (5)]. Kobe & Crawford (6) have listed certain thermodynamic properties for a wide variety of "petrochemicals," and Smith & Brown (7) have continued the excellent summaries of data published annually by *Industrial and Engineering Chemistry.*

Curl & Pitzer (8) have given extensive tables in terms of reduced temperature and reduced pressures by means of which the volumetric and thermodynamic properties of fluids can be estimated. Hirschfelder *et al.* (9) have used a modified principle of corresponding states as basis for a widely applicable equation of state, and have discussed the use of this equation in the calculation of thermodynamic functions of gases and liquids.

The *Thermochemical Bulletin* and the *Bulletin of Unpublished Thermal*

[1] The survey of the literature pertaining to this review was completed in December, 1958.

[2] The author is indebted to Mr. Arthur Gregory for assistance. The preparation of this review was aided by Research Grant G2855 from the National Science Foundation.

[3] Contribution No. 1527.

*Data*, previously circulated by the Calorimetry Conference of the U.S.A., have now been replaced by the *Bulletin of Chemical Thermodynamics*, which will be published annually with the support of the Commission on Thermodynamics of the International Union for Pure and Applied Chemistry. This publication, the first issue of which appeared during the year under review, promises to be of great usefulness.

## REACTION CALORIMETRY

The direct calorimetric determination of the heats of reactions other than combustion reactions has received increasing attention in recent years. The classical method of estimating the heats of chemical reactions is based on the application of Hess' law to combustion data. This method breaks down in numerous instances for one or more of the following reasons: (*a*) The quantity to be evaluated is the heat of reaction in solution, and the heats of solution and dilution needed for correcting the heat of reaction computed from the heats of combustion or formation of the pure reactants and products are not available. (*b*) The heat of reaction is so small that even the very high accuracy of modern combustion calorimetry is inadequate to give the desired accuracy in the heat of reaction. (*c*) One or more of the reactants or products may not be obtainable in sufficiently pure form to permit the determination of heats of combustion of adequate accuracy.

The effect of change in molecular structure on the heat of a reaction is frequently too small to be accurately evaluated from combustion data. Thus, the relatively small differences in the heats of hydrogenation of olefins of similar structure found in the classical work of Kistiakowsky & his colleagues (10, 10a), could not have been obtained from combustion experiments. The heat of mutarotation (11, 12) of $\alpha$-D-glucose to $\beta$-D-glucose in aqueous solution is only 280 cal./mole; to obtain this quantity with an accuracy of 10 per cent from combustion data and heats of solution would require an accuracy of 0.003 per cent in the combustion experiments. Many other reactions of interest in organic chemistry and biochemistry, for example, reactions involving proteins, illustrate the difficulties listed above.

It has been found in several instances that direct reaction calorimetry leads to interesting information in addition to the heat of reaction. For example, various authors have determined the kinetics of reactions by observing the rate of heat evolution or absorption. In a few cases, reaction heats have been employed to evaluate equilibrium constants and molecular weights.

In general, where reaction heats can be directly determined, they are obtained with better accuracy by this method than from combustion experiments or from measurements of the effect of temperature on equilibrium. On the other hand, reaction calorimetry is a less general method, and in numerous instances cannot be applied at all. Thus, the extensive information on the effect of structure on the heats of formation of isomeric hydrocarbons could only have been obtained by the combustion method since it is

impossible to carry out the individual isomerization reactions in a calorimeter.

The subject of reaction calorimetry has received very little attention in previous reviews in this series, and it seems useful to present a brief survey of the development of recent years in this field.

## Apparatus and Methods

Whereas a single design of bomb calorimeter is satisfactory for nearly all combustion experiments, a wide range of designs dictated in part by consideration of various experimental factors has been adopted for reaction calorimeters. It is evident, for example, that a calorimeter designed for observations on very slow reactions will incorporate certain features which are quite unnecessary in a calorimeter which is to be applied only to very rapid processes. We may list the following as the more important experimental factors to which attention must be given: the rate of the reaction; whether or not the kinetics of the reaction is to be studied in the calorimeter; the size of the heat effect; the cost or difficulty of obtaining the materials to be studied; the accuracy desired; the temperature range over which measurements are to be made; and the means of initiating the reaction in the calorimeter.

No systematic discussion of the design of reaction calorimeters from the point of view of experimental requirements has been given, and limitations of space prevent attempting such a discussion here. We shall merely refer briefly to several reaction calorimeters which have been shown to be useful.

One of the earliest reaction calorimeters was described by Tian (13). This calorimeter employed Peltier cooling and Joule heating for compensating the chemical heat effects to be studied. The rate of heat loss from the reaction cell was measured by a multijunction thermocouple and the uncompensated heat evaluated by integration of the temperature-time curve. The Tian calorimeter has been further extensively developed by Calvet & his colleagues (14) and by Attree *et al.* (15). It is particularly well adapted to the study of slow heat effects although it may also be used for processes of short duration.

Kitzinger & Benzinger (16) have employed a calorimeter of the heat-leak type in which a very rapid heat transfer from reaction solution to measuring thermocouple takes place, so that efficient utilization of the thermocouple output is achieved even with processes of short duration, for which the apparatus is particularly well suited.

Sturtevant (11, 17) has described three calorimeters designed primarily for the measurement of the heats and rates of slow reactions. The most recent of these employs the twin calorimeter procedure with continuous electrical compensation of chemical heats. A calorimeter briefly described by Charuel & Traynard (18) also employs automatic feedback of electrical heat for compensation.

A calorimeter has been described by Kistiakowsky *et al.* (10) for the

determination of heats of hydrogenation of unsaturated compounds in the gas phase, and has been employed in an extensive series of experiments. Bent & co-workers (19), and later Williams (20), employed Dewar calorimeters for the determination of heats of hydrogenation in solution. More recently, Turner & co-workers (21) and Flitcroft, Skinner & Whiting (22) have also described instruments for this purpose; the latter instrument employs particularly vigorous agitation of the reaction mixture. Pedley, Skinner & Chernick (23) and Brown & Gintis (24) described calorimeters suitable for gas-liquid reactions in which the solubility of the gaseous reactant is high enough so that vigorous stirring is not needed. Lacher & his co-workers (25, 26) have utilized an ingenious isothermal calorimetric method for the determination of heats of hydrogenation, halogenation and hydrohalogenation.

The Bunsen ice calorimeter, and modifications utilizing other working substances such as diphenyl ether (m.p., 26.9°), are well suited to the calorimetry of slow processes since the heat-leak corrections in this type of calorimeter can be made very small. Dainton *et al.* (27) have employed a diphenyl ether calorimeter in the determination of heats of polymerization. Butcher & Nickson (28) have used an ice calorimeter in the study of the hydration of olefins.

Borchardt & Daniels (29) have recently discussed the application of differential thermal analysis to the determination of reaction rates and heats. Kröger & Janetzko (30) [see also Prosen, Johnson & Pergiel (260)] made an important contribution when they showed that reliable values for the heats of slow reactions at very high temperatures can be obtained by a calorimeter in which reactions are initiated by very rapid elevation of the temperature by an accurately measured amount of electrical energy.

Among other calorimeters which have been designed in recent years for various purposes, we may mention those of Brown & Horowitz (31), Holmes & Tyrrall (32), Pritchard & Skinner (33), and Skinner & Smith (34). Sunner & Wadsö (35), after a careful study of the problems involved, arrived at a design particularly suited for reactions of moderately long duration and heat changes amounting to 0.5 cal. or less per ml.

## Applications

*Heats of hydrogenation, halogenation, and hydrohalogenation.*—Mention has been made of the determination of heats of hydrogenation by Kistiakowsky & his colleagues (10, 10a). The data obtained in this work have been extremely useful, for example, in the estimation of resonance energies. It is fortunate that other laboratories are continuing this type of work. Turner & his associates (21, 36, 37, 38) have determined the heats of hydrogenation (in solution) of a large number of compounds, including some nonbenzenoid aromatic compounds (39). Skinner *et al.* (22, 40) have also recently initiated determinations of heats of hydrogenation. Lacher & his co-workers (26, 41) have performed an extensive series of measurements of the heats of hydro-

genation of saturated and unsaturated organic halides; in most of these cases the reaction includes replacement of halogen atoms by hydrogen. Carson & Carter (42) have recently studied the reaction of alkyl iodides with LiH to obtain data from which heats of formation of alkyl iodides can be obtained. Jackman & Packham (43) have reported heats of hydrogenation reactions brought about by $LiAlH_4$.

In many instances, the heat of addition of halogen or hydrohalogen to unsaturated compounds gives information which can be utilized in the same manner as heats of hydrogenation. Conn, Kistiakowsky & Smith (44) and Lister (45) reported the heats of addition of halogens to a variety of substances. More recently, Lacher *et al.* (25, 46) have reported numerous heats of halogenation and hydrohalogenation.

Few halogen substitution reactions have been investigated calorimetrically. Aside from perfluorination reactions (47) and combustions in fluorine gas (48), most halogen substitution reactions are insufficiently cleancut for thermochemical study. An exception is provided by the reaction of halogens with organometallic compounds. Skinner *et al.* (49) have determined the heats of reaction of $Br_2$ or $I_2$ with various zinc, cadmium, mercury, and tin alkyls, and Ubbelohde & co-workers (50) have studied the reaction of $I_2$ (and HI) with Grignard reagents. One important application of halogenation experiments has been the estimation of the heats of formation of various alkyl halides with an accuracy exceeding that obtainable from presently available combustion data.

*Heats of hydrolysis.*—The heats of hydrolysis of many inorganic and organic compounds have been determined in the past decade. Particular mention may be made of the extensive data coming from the laboratories at Manchester (33, 34, 51) and Lund (52 to 55), which have yielded heats of formation for a wide range of inorganic and organic acid derivatives.

*Heats of ionization.*—In general direct calorimetry affords the most accurate method for the determination of heats of ionization. Canady, Papée & Laidler (56) have studied six organic acids by this method. Various heats of ionization have been determined (57, 58, 59) in connection with other investigations.

*Heats of polymerization.*—Considerable attention has been given in recent years to the calorimetric determination of heats of polymerization. Tong & Kenyon (60), Ekegren & co-workers (61), and Dainton *et al.* (27) have employed the method of isothermal calorimetry. Ordinary calorimetry has been applied by Baxendale & Madaras (61a), and Evans & Tyrrall (62). Bengough (63) and Suzucki *et al.* (64) have made use of the fact that the central portion of a mass of polymerizing material is adiabatic for several seconds after the commencement of polymerization.

*Heats of formation of co-ordination compounds.*—Brown & his colleagues (24, 31, 65) have published an extensive series of determinations of heats of formation of co-ordination compounds. These data have been primarily used

in the study of steric interaction energies. Recent work in this field has been reported by Greenwood *et al.* (66) and Staveley (67).

*Miscellaneous.*—Neale & Williams (68) and Chernick, Skinner & Mortimer (69) have determined the heats of esterification of $PCl_3$ by alcohols. Chernick & Skinner (70) studied the oxidation by $H_2O_2$ of tripropylphosphine, tributylphosphine, and triethyl phosphite; Chernick, Pedley & Skinner (71) studied the addition of sulfur to these compounds.

## Special Applications

*Determination of equilibrium constants.*—Since the heat observed for a reaction is proportional to the extent to which the reaction has progressed (in the absence of disturbing factors arising, for example, from changes with concentration in the partial molal heat contents of dissolved species), it is evident that calorimetric measurements, in suitable cases, can be utilized for the determination of equilibrium constants. Sturtevant (11) applied this method to the mutarotation of glucose. More recently, Benzinger (72) discussed the method in general terms, and he & Hems (73) applied it to the hydrolysis of glutamine. Sturtevant, Rice & Geiduschek (74) employed the calorimetric method to estimate equilibrium constants for the acid denaturation of deoxyribose nucleic acid.

*Determination of molecular weights.*—Standard enthalpy changes computed from the temperature variation of equilibrium constants (determined either calorimetrically or by more usual methods) are obtained in units of calories per mole; comparison of these with direct calorimetric enthalpies in calories per gram lead to estimates of molecular weights. Such estimates are potentially of considerable value in complex systems. Barcroft & Hill (75) in 1910, and Brown & Hill (76) in 1923, applied this procedure to hemoglobin. A recent application is reported by Sturtevant *et al.* (74) who concluded that the "denaturing unit" in deoxyribose nucleic acid is very much smaller than the deoxyribose nucleic acid molecule.

*Determination of rates of reactions.*—In view of the proportionality between heat and extent of reaction, a general method of reaction rate determination is afforded by reaction calorimetry (77, 78). The recent literature includes several examples of this application (57, 59, 79 to 82). In many instances rate data have been obtained incidentally in investigations directed primarily toward the evaluation of reaction heats, but in some cases the calorimetric rate data were of importance in analyzing the heat data.

*Biochemical processes.*—A series of measurements on enzymic hydrolyses of synthetic peptides (81, 83) and a synthetic polypeptide (57) have furnished typical values for the heats of hydrolysis of peptide and amide bonds. In one case (83) the equilibrium of peptide hydrolysis was also observed. These data are of significance in connection with the thermodynamics of protein biosynthesis. The heats of enzymic hydrolysis of inorganic pyrophosphate (84) *p*-nitrophenylphosphate (85) and of adenosinetriphosphate (58, 86) have also been reported.

The enthalpy change accompanying the transfer of a methyl group from dimethylacetothetin to homocysteine to form methionine was reported by Durell & Sturtevant (59). A reasonable estimate of the standard entropy change to be expected led to a value for the otherwise inaccessible standard free energy for this biochemically important reaction.

The heats of a number of complex reactions (i.e., reactions in which the structural changes occurring are not well understood) have been determined. Although in such cases thermal data are not directly interpretable, as they are in the cases of simpler reactions, it may be expected that calorimetric data will prove of help in arriving at a better understanding of the reactions. Canady & Laidler (87) have recently determined the heat of combination of the enzyme α-chymotrypsin with hydrocinnamic acid, and from a comparison of this heat with apparent heats derived from the temperature coefficient of the rate of hydrolysis of the ethyl ester by chymotrypsin have drawn interesting conclusions concerning the enzyme mechanism. Steiner & Kitzinger (88) determined the heat of the interaction between human serum albumin and its rabbit antibody. Sturtevant *et al.* have studied the denaturation of pepsin (17) and of deoxyribose nucleic acid (74), the interaction between trypsin and the soybean trypsin inhibitor (89), and isomerization of bovine serum albumin at low *p*H (82), and the polymerization of fibrin monomer (80).

*Biological thermogenesis.*—Calvet & Prat (14) have employed the Tian-Calvet (13) microcalorimeter in the determination of the evolution of heat under various circumstances by various biological systems, including vegetable systems, microorganisms, invertebrates, and vertebrates. In recent publications, Prat has discussed the details of the "thermograms" (continuously recorded plots of heat evolution in calories per hour vs. time) produced by various insects (90) and newborn mice (91).

## TABULAR SUMMARIES

Table I lists publications giving thermochemical and thermodynamic information for inorganic substances, and Table II lists publications concerning organic substances. Organometallic compounds (except for certain addition compounds with gallium halides) are included in Table II. Miscellaneous groups of organic compounds are included in Table III. In each Table, the properties and reactions are indicated by the *Code to Properties* given below; in most cases the reactions for which data are given are indicated by listing the reactants or by a suitable abbreviation.[4]

[4] Dec., decomposition; disprop., disproportionation; dissoc., dissociation; enol., enolization; ioniz., ionization; isom., isomerization; oxid., oxidation; polym., polymerization, including dimerization; etc.

TABLE I

INORGANIC COMPOUNDS

| Substance | Property | Reference | Substance | Property | Reference |
|---|---|---|---|---|---|
| Air (high temp.) | aefg | (92) | ClF | bj | (117) |
| He | ae | (93 to 96) | $ClF_3$ | abhj | (117, 118) |
| $^3He$ | ef | (97) | $FClO_3$ | bcef | (119) |
| He—$CO_2$ mixtures | a | (94) | $Br_2$ | bcefh | (120) |
| | | | $Br_2+Br^-$ | lmn | (121) |
| He—$N_2$ | a | (95) | BrF | bj | (117) |
| Ne | a | (93) | $BrF_3$ | abhj | (117, 118) |
| A | ae | (93, 98) | $BrF_5$ | ab | (117) |
| Kr | ac | (93, 99) | $I_2$ | c | (122) |
| Xe | a | (93) | $IF_5$ | abj | (117) |
| $O_2$ | e | (100) | $IF_7$ | ab | (117) |
| $O_2^-$ | f | (101) | S | abem($SO_2$) | (123 to 126) |
| $O_3$ | e | (102) | $H_2S$, $D_2S$ | ij | (127) |
| $H_2$, HD, $D_2$ | c | (103) | $H_2S_2$ | bcde | (128, 129) |
| $H_2$—$D_2$, $H_2$—HD mixtures | ac | (103) | $H_2S_3$ | bcd | (128) |
| | | | $H_2S_4$ | bcd | (128) |
| $OH^-$ | f | (101) | $H_2S_5$ | bcd | (128) |
| $H_2O$ | adeq | (104 to 108) | SO | j | (126) |
| $H_2O$ (high pressure) | a | (109, 110) | $SO_2$ | m(S) | (126) |
| | | | $H_2SO_3$ | q | (130, 131) |
| $^1H^3HO$ | c | (111) | $HSO_4^-$ | q | (132) |
| $H_2O_2$ | ceg | (112, 113) | $SO_2Cl_2$ | j | (133) |
| $F_2$ | mnp | (114) | $H_2Se$ | q | (134) |
| HF | l($NH_3$; polym.) | (115, 146) | Te | c | (135, 136) |
| | | | $H_2TeO_4$ | q | (136a) |
| $HF_2^-$ | f | (101) | $N_3$ | afh | (93, 95, 137) |
| $H_4F_4$ | l(dissoc.) | (115) | $^{14}N_2$, $^{14}N^{15}N$, $^{15}N_2$ | c | (138) |
| $H_6F_6$ | l(dissoc.) | (115) | $N_3^-$ | f | (101) |
| $ClO_2$ | ln($H_2O_2$) | (116) | NO | h | (139) |

*Code to Properties in Tables I, II and III*

a. Compressibility, density, equation of state
b. Data for transitions
c. Vapor pressure, heat of vaporization or sublimation
d. Data pertaining to the critical state
e. Heat capacity
f. Entropy or entropy increment
g. Enthalpy or enthalpy increment
h. Thermodynamic functions [usually $C_p^0$, $S^0$, $(H^0-H_0^0)/T$, $-(F^0-F_0^0)/T$]
i. Heat of combustion
j. (Standard) enthalpy of formation
k. (Standard) free energy of formation
l. Heat of a reaction
m. Equilibrium data for a reaction
n. Standard free energy of a reaction
o. Dissociation pressure
p. Dissociation energy or enthalpy
q. Thermodynamics of ionization in solution
r. Isotopic exchange equilibria

TABLE I (*continued*)

| Substance | Property | Reference |
|---|---|---|
| $^{14}N^{16}O$, $^{15}N^{16}O$, $^{14}N^{18}O$ | c | (138) |
| $NO^+$ | f | (101) |
| $NO_2^+$ | fj | (101, 140) |
| $N_2O$ | r | (141) |
| $N_2O_4$ | l,n(dissoc.) | (142) |
| $NH_3$ | cefghl (dec.; HF) | (143 to 146) |
| $ND_3$ | efh | (144) |
| $NH_4^+$ | f | (101) |
| $N_2H_2$ | jkl($H_2$) | (147, 148) |
| $N_2H_4$ | lp | (147, 148) |
| $NH_4HF_2$ | j | (146) |
| $NO_2ClO_4$ | j | (140) |
| $NH_4IO_3$ | j | (149) |
| $NH_4ICl_4$ | o | (150) |
| $(NH_4)_2SO_4$, $(ND_4)_2SO_4$ | e | (151) |
| $PH_3$, $PD_3$ | efh | (144) |
| $PH_4^+$ | f | (101) |
| $H_3PO_4$ | q | (152. 153, 154) |
| $PBr_3$ | almo | (155) |
| $AsH_3$, $AsD_3$ | efh | (144) |
| $As_2O_3$ | l($O_2$) | (156) |
| $AsF_5$ | b | (117) |
| $SbH_3$, $SbD_3$ | efh | (144) |
| $SbF_5$ | ab | (117) |
| Bi | ef | (157, 158) |
| C(diamond) | e | (159, 160) |
| C(graphite) | ce | (161 to 166) |
| CO | p | (161) |
| $CO_2$ | a | (94) |
| $H_2CO_3$ | q | (131) |
| CCl | eghk | (167) |
| $CN^-$ | f | (101) |
| $C_4N_2$ | i | (168) |
| $OCN^-$ | f | (101) |
| $SCN^-$ | f | (101) |
| $Si_n$ | chl | (169) |
| $SiF_4$ | e | (170) |
| $SiCl_4$ | d | (171) |
| $Si_mC_n$ | chlop | (169) |
| $GeO_2$ | bcefmnop | (172, 173, 174) |
| $H_2GeO_3$ | q | (175) |
| GeS | c | (176) |
| $GeS_2$ | mo | (177) |
| Sn | e | (178) |
| SnS | befg | (179) |
| $SnS_2$ | efg | (179) |
| Pb | e | (180) |
| PbO(red) | ef | (181) |
| PbO(yellow) | ef | (181) |
| $Pb_2O_3$ | ef | (181) |
| $PbBr_2$ | bc | (182) |
| $Pb(NO_3)_2$ | j | (183) |
| $Ga_2O_3$ | ef | (173) |
| $GaCl_3$ | l(organic compounds) | (67) |
| $GaBr_3$ | l($C_5H_5N$) | (67) |
| $GaI_3$ | c | (184) |
| GaSb | j | (185) |
| $Ga_2C_2$ | j | (186) |
| In | c | (187) |
| InCl | e | (184) |
| $InCl_3$ | c | (184) |
| $InBr_3$ | c | (184) |
| $InI_3$ | c | (184) |
| InSb | bej | (185, 188) |
| Zn | e | (189) |
| ZnO | lmn($H_2O$) | (190) |
| $ZnCl_2$ | bc | (182) |
| $ZnBr_2$ | bc | (182) |
| $ZnAs_2$ | c | (191) |
| $CdBr_2$ | bc | (182) |
| $CdI_2$ | bc | (182) |
| Cu | e | (192) |
| CuI | e | (193) |
| $Cu(NO_3)_2$ | c | (194) |
| $Cu_xGe_y$ | e | (195) |
| Ag | e | (192) |
| AgCl | bc | (182, 196) |
| AgBr | bc | (182, 196) |
| AgI | e | (193) |
| $Ag(CN)_2^-$ | f | (101) |
| $Ag_xCd_y$ | hj | (197, 198) |
| $Ag_xCu_y$ | j | (199) |
| $Au(CN)_2^-$ | f | (101) |
| $AuCu_3$ | e | (200) |
| $Au_xCu_y$ | j | (199) |
| $Au_xAg_y$ | j | (199) |
| Pu | be | (201) |
| $PuO_2$ | ij | (202) |
| Pt | e | (203) |
| Re | l($HNO_3$) | (204) |
| $HReO_4$ | jl($NH_3$) | (204) |
| $H_2ReCl_6$ | jl($H_2O_2$) | (204) |
| $(NH_4)_2ReCl_6$ | jl($AgNO_3$; CsCl) | (204) |
| $Ag_2ReCl_6$ | j | (204) |
| Pd | ce | (205, 206) |
| Ni | e | (203) |
| NiO | befg | (207) |
| $NiF_2$ | c | (208) |
| $Ni(CO)_4$ | hij | (209, 210) |
| $NiTe_x$ | efho | (211, 212) |
| CoO | efg | (207) |
| $Co_2O_4$ | efg | (207) |
| $Fe_2O_3$ | n | (213) |
| $Fe_3O_4+O_2$ | n | (213) |
| $FeCl_2$ | cklmn(polym.) | (214, 215) |
| $Fe_2Cl_4$ | lmn(dissoc.) | (215) |
| $Fe_2Cl_6$ | k | (214) |
| FeSx | be | (216) |
| $ZnFe_2O_4$ | efh | (217) |
| $CuFe_2O_4$ | be | (218) |
| MnO—CoO | e | (219) |

TABLE I (*continued*)

| Substance | Property | Reference |
|---|---|---|
| $Mn_4N$ | ij | (220) |
| $Mn_6N_2$ | ij | (220) |
| $Mn_2(CO)_{10}$ | ij | (221) |
| $Cr_2O_7^{--}$ | jkl($H_2O$) | (222) |
| $HCrO_4^-$ | jkq | (222) |
| $Cr(OH_2)_6^{3+}$ | l($Cl^-$) | (223) |
| $CrF_2$ | befh | (224) |
| $CrCl_3$ | befh | (224) |
| $Cr(OH_2)_5Cl^{++}$ | l($Cl^-$) | (223) |
| $Ni_xCr_yFe_z$ | eg | (225) |
| $MoO_2$ | cefl | (173, 226) |
| $MoO_3$ | cl | (226) |
| $Mo_4O_{11}$ | cl | (226) |
| $Mo_2Si$ | efg | (227) |
| $PbMoO_4$ | j | (183) |
| W | efm($H_2$, $WO_2$, $H_2O$) | (157, 228) |
| $WO_2$ | clm($H_2$, W, $H_2O$) | (226, 228) |
| $WO_3$ | cl | (226) |
| $W_mO_n$ | j | (228) |
| $PbWO_4$ | e | (229, 230) |
| $ZnWO_4$ | e | (229) |
| $CdWO_4$ | e | (229, 230) |
| $Ag_2WO_4$ | j | (231) |
| $NiWO_4$ | ej | (229, 232) |
| $MnWO_4$ | j | (232) |
| U | e | (233) |
| $UO_2$ | cl(oxid.)p | (234, 235) |
| $UO_2^+$ | f | (101) |
| $UO_{2+x}$ | lno | (236) |
| $U_3O_8$ | ijl | (202, 235) |
| $U_4O_9$ | l(oxid.) | (235) |
| $VF_5$ | b | (117) |
| $VOF_3$ | c | (237) |
| Nb | e | (238) |
| $NbO_2$ | efij | (173, 239) |
| $NbF_5$ | ab | (117) |
| $NbCl_5$ | j | (240) |
| $Nb_2N$ | ij | (239) |
| Ta | efg | (241, 242) |
| $TaF_5$ | ab | (117) |
| $TaCl_5$ | j | (240) |
| $Ta_2N$ | ij | (239) |
| Ti | el($Br_2$) | (243, 244, 248) |
| $TiO_2$ | eg | (245) |
| $TiF_4$ | cf | (246) |
| $TiCl_2$ | cj | (247) |
| $TiCl_3$ | fj | (247) |
| $TiCl_4$ | cdj | (171, 248, 249) |
| $TiBr_3$ | fjl($Hg_2Br_2$) | (250) |
| $TiBr_4$ | cjf | (248, 251) |
| TiOCl | j | (252) |
| TiC | j | (186) |
| Zr | e | (243, 253, 254) |
| $Zr_xH_y$ | eln | (253, 254) |
| $ZrF_4$—LiF mixtures | c | (255) |
| $ZrCl_4$ | bc | (256) |
| $ZrN_x$ | jk | (257) |
| Hf | e | (243) |
| $HfCl_4$ | c | (256) |
| $ThF_4$ | c | (258) |
| B | l | (259) |
| $BH_4^-$ | f | (101) |
| $B_2H_6$ | cjp | (260, 261) |
| $B_5H_9$ | cjp | (260, 262) |
| $B_2O_2$ | m(dissoc.) | (263) |
| $B_2O_3$ | cfjl($H_2O$), m(B) | (259, 263, 264, 265) |
| $BF_3$ | elm($F^-$) | (170, 266, 267) |
| $BF_4^-$ | f | (101) |
| $BCl_3$ | l(organic compounds) | (67) |
| $B_2Cl_4$ | be | (268) |
| $AlH_4^-$ | f | (101) |
| $Al_2O_3$ | eg | (269) |
| $AlCl_3$ | cj | (270, 271) |
| $AlCl_3 \cdot 6H_2O$ | j | (270) |
| $AlCl_4^-$ | f | (101) |
| $AlBr_3$ | c | (271) |
| $Al_2Br_2Cl_4$ | c | (271) |
| $AlPO_4$ | j | (272) |
| $Al_2C_2$ | j | (186) |
| Tb | e | (273) |
| Gd | e | (273) |
| Ce | b | (274) |
| La | e | (275) |
| $LaC_2$ | j | (186) |
| $(NH_4)_2BeF_4$, $(ND_4)_2BeF_4$ | e | (151) |
| $BeC_2$ | j | (186) |
| $BaMoO_4$ | e | (229) |
| $Mg_xAl_y$ | e | (276) |
| $MgSO_4$ | e | (277) |
| $MgMoO_4$ | e | (229) |
| Ca | em($BaCl_2$) | (278, 279) |
| $CaMoO_4$ | j | (183) |
| $SrMoO_4$ | e | (229) |
| $SrWO_4$ | e | (229) |
| Li | l($H_2O$) | (280) |
| LiH, LiD | jl($H_2O$) | (280) |
| LiF | celmn(polym.) | (255, 281, 282, 283) |
| LiF—$ZrF_4$ mixtures | c | (255) |
| $Li_2F_2$ | lmn(dissoc.) | (281) |
| $Li_2F_2$ | lmn(dissoc.) | (281) |
| $Li_2Cl_2$ | ln(dissoc.) | (284) |
| LiBr | b | (285) |
| $Li_2Br_2$ | ln(dissoc.) | (284) |
| LiS | j | (286) |
| $Li_2SO_4$ | b | (287) |
| $Li_{.05}Zn_{.95}Fe_{2.05}O_4$ | efh | (217) |
| Na | l($H_2O$) | (280) |

TABLE I (*continued*)

| Substance | Property | Reference | Substance | Property | Reference |
|---|---|---|---|---|---|
| NaH, NaD | jl($H_2O$) | (280) | $NaLiF_2$ | lmn | (281) |
| NaOH | clmo | (288, 289, 290) | K | l($H_2O$) | (280) |
| $Na_2(OH)_2$ | lmn(dissoc.) | (289, 290, 291) | KH, KD | jl($H_2O$) | (280) |
| NaF | cjlmn(polym.) | (281, 282, 292) | KOH | clmn | (289, 291) |
| $NaHF_2$ | lno | (293) | $K_2(OH)_2$ | lmn(dissoc.) | (289, 291) |
| $Na_2F_2$ | lmn(dissoc.) | (281, 284) | KF | c | (282) |
| $Na_2Cl_2$ | ln(dissoc.) | (284) | KCl | ce | (282, 294) |
| NaBr | bc | (182, 285) | $K_2Cl_2$ | ln(dissoc.) | (284) |
| $NaBrO_3$ | j | (149) | KBr | be | (285, 294) |
| NaI | e | (294) | KI | e | (283, 294) |
| $Na_2I_2$ | ln(dissoc.) | (284) | $K_2I_2$ | ln(dissoc.) | (284) |
| $Na_2S$ | fjkm($CO_2$) | (295) | $KICl_4$ | o | (150) |
| $Na_2SO_4$ | bjm(C) | (287, 295, 296) | $K_2SO_4$ | b | (287) |
| $Na_2SO_4 \cdot 10H_2O$ | efl(dissoc.) | (297) | $K_2CrO_4$ | j | (222) |
| $Na_2S_2O_7$ | b | (298) | $K_2Cr_2O_7$ | j | (222) |
| $NaNO_3$ | be | (299) | $KBH_4$ | eh | (301) |
| $NaFeO_2$ | efg | (269) | $KNa(OH)_2$ | lmn | (291) |
| $Na_2WO_4$ | j | (231) | RbF | c | (255, 282) |
| $Na_xWO_3$ | e | (300) | RbF—$ZrF_4$ mixts. | c | (255) |
| $NaBH_4$ | eh | (301) | $Rb_2Cl_2$ | ln(dissoc.) | (284) |
| $Na_2B_2O_4$ | j | (302) | $RbICl_4$ | o | (150) |
| $Na_2B_4O_7$ | ej | (302, 303) | CsF | c | (282) |
| $Na_{2.96}AlF_{5.96}$ | j | (292) | $Cs_2SO_4$ | b | (287) |
| $Na_2O \cdot 8CaO$ $3Al_2O_3$ | j | (296) | $CsNO_3$ | be | (304) |
| | | | $Cs_2ReCl_6$ | j | (204) |

## TABLE II

ORGANIC COMPOUNDS

| Substance | Property | Reference |
|---|---|---|
| Abietic acid | q | (305) |
| Acetaldehyde thiosemicarbazide | ij | (306) |
| Acetic acid | lm(polym.)q | (56, 307, 308) |
| Acetic acid *n*-mer | m(dissoc.) | (308) |
| Acetic anhydride | l($BuNH_2$) | (309) |
| Acetoacetate | lmn(enol.) | (310) |
| Acetone | l(enol.) | (52) |
| Acetone thiosemicarbazide | ij | (306) |
| Acetophenone | i | (311) |
| Acetosuccinic acid | q | (312) |
| Acetyl radical | jln | (313, 314) |
| Adenosinetriphosphate | mn($H_2O$) | (315) |
| Adenylosuccinic acid | kmn($H_2O$) | (316) |
| Aminobenzoic acids (*o*, *m*, *p*) | q | (317) |
| Anisole | cd | (318) |
| Arachin | lmn(dissoc.) | (319) |

TABLE II (*continued*)

| Substance | Property | Reference |
|---|---|---|
| Benzene | acd | (318, 320, 321) |
| 2,3-Benzo-1,4-dioxacycloheptane | ci | (322) |
| Benzoic acid | fhikl(ioniz.)q | (56, 323, 324, 325) |
| Benzophenone | i | (326) |
| Bicyclo(2:2:1)heptadiene-2,5 | i | (327) |
| Bovine serum albumin | l(isom., ioniz.) | (82) |
| 1-Butanethiol | cij | (328) |
| 2-Butanethiol | abcehij | (328, 329) |
| *n*-Butyl acetate | l($H_2O$) | (55) |
| *t*-Butyl alcohol | m(polym.) | (330) |
| *t*-Butyl alcohol *n*-mer | m(dissoc.) | (330) |
| Butylamine | cd | (318) |
| *p*-*t*-Butylbenzophenone | i | (326) |
| *t*-Butyl bromide | f | (331) |
| *t*-Butyl chloride | h | (332) |
| *t*-Butylphenylketone | i | (311) |
| *n*-Butyl thiolacetate | l($H_2O$, $BuNH_2$) | (54, 309) |
| *t*-Butyl thiolacetate | l($H_2O$) | (54) |
| Butyric acid | cl(ioniz.) | (56, 122) |
| Carbon disulfide | amn(S) | (333, 334, 335) |
| Carbon monosulfide | jmn(dissoc.) | (335) |
| Carbon tetrachloride | aceghkm($AlCl_3$) | (167, 321, 334, 336) |
| Carbon tetrafluoride | abe | (170, 337) |
| Carbon tetraiodide | h | (338) |
| Catecholdisulfonic acid | q | (339) |
| Cellobiose | ln(isom.) | (12) |
| Chloroform | c | (321) |
| Chromium diphenyl | i | (340) |
| Chymotrypsin | l(hydrocinnamic acid.) | (87) |
| Citric acid | ij | (341) |
| Copper acetonylacetonate | e | (342) |
| Cresols(*o*, *m*, *p*) | cd | (318, 343) |
| Cumene | cd | (318) |
| Cyclodecanone | i | (327) |
| Cycloheptanone | i | (327) |
| Cyclohexane | acd | (318, 321, 334) |
| Cyclohexanol | cd | (318) |
| Cyclohexanone | cd | (318) |
| Cyclopentane | ef | (344) |
| Cyclopentane—2,2-dimethylbutane mixtures | bce | (345) |
| Cyclopropane | cd | (346) |
| Cyclopropyl cyanide | h | (347) |
| Decalin | cdhklmn(isom.) | (318, 348) |

TABLE II (*continued*)

| Substance | Property | Reference |
|---|---|---|
| Dehydroabietic acid | q | (305) |
| Deoxyribose nucleic acid | lmn(isom.) | (74) |
| Dibenzofuran | ci | (349) |
| Dibenzopyran | ci | (349) |
| 3,5-Dibromophenol | q | (350) |
| 3,5-Dibromo-4-dimethylsulfoniophenol ion | q | (350) |
| Di-*t*-butylethylene | l($H_2$) | (38) |
| Dibutyl formal | il(polym.) | (351) |
| Dibutyl phthalate | c | (352) |
| Dibutyl sebacate | c | (352) |
| *o*-Dichlorobenzene | ij | (353) |
| 3,5-Dichloro-4-dimethylsulfoniophenol ion | q | (350) |
| 1,2-Dichloroethanol | ij | (353) |
| 1,1-Dichloroethylene | ijl(polym.) | (353) |
| 3,5-Dichlorophenol | q | (350) |
| 2,5-Dichlorostyrene | ij | (353) |
| p-Diethylbenzene | lmn($C_6H_6$) | (367a) |
| Diethylenetriaminepentacetic acid | q | (354) |
| Diethyl ether | a | (333) |
| Diethyl nitramine | ij | (355) |
| Difluorochlorodeuteromethane | h | (356) |
| Difluorochloromethane | h | (356) |
| Difluorodichloromethane | m($AlCl_3$) | (336) |
| Dihydropyran | ci | (349) |
| 1,8-Dihydroxy-2-(2-hydroxyphenyl)-3,6-naphthalenedisulfonic acid | q | (357) |
| Diisopropylbenzene | cd | (318) |
| *o*-Dimethoxybenzene | ci | (322, 358) |
| Dimethylacetothetin | l(homocysteine) | (59) |
| 2,2-Dimethylbutane—cyclopentane mixtures | bce | (345) |
| Dimethylene formal | il(polym.) | (351) |
| N,N-Dimethylglycine | q | (359) |
| Dimethyl nitramine | ij | (355) |
| 2,4-Dimethylpentene-1 | l($H_2$) | (38) |
| 2,4-Dimethylpentene-2 | l($H_2$) | (38) |
| 4,4-Dimethylpentene-2 | l($H_2$) | (38) |
| *p*-Dimethylsulfoniophenol ion | q | (350) |
| 2,2-Dinitropropane | b | (360) |
| 1,3-Dioxaindane | ci | (322) |
| 1,3-Dioxane | ci | (358) |
| 1,4-Dioxane | cd | (318) |
| Dioxatetrahydronaphthalene | ci | (322) |
| 1,3-Dioxolane | ci | (358) |
| Diphenyl | cd | (318) |

TABLE II (*continued*)

| Substance | Property | Reference |
|---|---|---|
| N,N′-Diphenylacetamidine | c | (361) |
| Diphenylamine | cd | (318) |
| Diphenylcarbonate | efhijkn($H_2O$) | (362) |
| Diphenyl ether | cd | (318) |
| Diphenylmethane | cd | (318) |
| Diphosphopyridine nucleotide | mn($C_2H_5OH$) | (363) |
| 2,3-Dithiabutane | cefhijk | (364) |
| 3,4-Dithiahexane | efhijk | (364) |
| 4,5-Dithiaoctane | bcefhijk | (364) |
| *n*-Dodecane | l($Cl_2$, $SO_2+Cl_2$) | (365) |
| Ephedrinium ions | q | (366) |
| Ethane | a | (337) |
| Ethyl acetate | l($H_2O$) | (55) |
| Ethyl alcohol | m($H_2SO_4$) | (367) |
| Ethylbenzene | lmn(disprop.) | (367a) |
| *p*-Ethylbenzophenone | i | (326) |
| 1-Ethylcyclopentene | l($H_2$) | (37) |
| 1-Ethylcyclohexene | l($H_2$) | (37) |
| Ethylene | a | (337) |
| Ethylenediamine-tetraacetic acid | q | (368) |
| Ethylene dibromide | c | (369) |
| Ethyl formate | aelm(isom.) | (370) |
| Ethylidenecyclopentane | l($H_2$) | (37) |
| Ethylidenecyclohexane | l($H_2$) | (37) |
| *p*-Ethylthiobenzoic acid | q | (371) |
| Ethyl thiolacetate | l($H_2O$) | (54) |
| Fluorobenzene | acd | (372) |
| Fluorodichlorodeuteromethane | h | (356) |
| Fluorodichloromethane | h | (356) |
| Fluoroform | ij | (373) |
| Fluorotrichloromethane | m($AlCl_3$) | (336) |
| Formamide | ehjk | (374) |
| Formic acid | fl(ioniz.)q) | (56, 307, 375) |
| Fumaric acid | ij | (376) |
| Gallium methyl iodide | j | (377) |
| Gallium trimethyl | jl($I_2$) | (377) |
| Glucosamine | q | (378) |
| D-Glucose | ln(isom.) | (12) |
| L-Glutamic acid | i | (379) |
| L-Glutamine | i | (379) |
| Glycerol-1-phosphate | q | (380) |
| Glycine | q | (359) |
| Hexachlorobenzene | efhijk | (353, 381) |
| Hexacyclo(7:2:1:$0^{2,5}$:$0^{3,10}$:$0^{4,8}$:$0^{6,12}$) dodecane | ij | (382) |

TABLE II (*continued*)

| Substance | Property | Reference |
|---|---|---|
| *n*-Hexane | acd | (318, 321, 333) |
| L-Homocysteine | l(Me$_2$acetothetin) | (59) |
| Hydrazinium thiocyanate | ij | (306) |
| Hydroquinone | q | (383) |
| Imidazole | q | (384) |
| Iodobenzene | lmn(Cl$_2$) | (385) |
| Iodoform | h | (338) |
| Isobutylphenylketone | i | (311) |
| Isobutyric acid | l(ioniz.) | (56) |
| Isocitric acid | q | (386) |
| Isonicotinic acid | q | (387) |
| Isophthalic acid | q | (388) |
| Isopropenyl acetate | l(H$_2$O) | (52) |
| Isopropyl acetate | l(H$_2$O) | (55) |
| *p*-Isopropylbenzophenone | i | (326) |
| Isopropyl nitrate | c | (389) |
| *p*-Isopropylthiobenzoic acid | q | (371) |
| Isopropyl thiolacetate | l(H$_2$O) | (54) |
| Lactose | ln(isom.) | (12) |
| Lauric acid | cq | (352, 390) |
| L-Leucine | i | (379) |
| 2,6-Lutidine | ac | (320) |
| Maleic acid | ij | (376) |
| Maltose | ln(isom.) | (12) |
| Mercury diphenyl | c | (391) |
| Methane | a | (392) |
| Methanol | q | (393) |
| Methanol dimer | p | (394) |
| Methanol tetramer | p | (394) |
| Methemoglobin azide | lmn(dissoc.) | (395) |
| Methemoglobin nitrite | lmn(dissoc.) | (396) |
| Methacrylonitrile | ln(polym.) | (369a) |
| *p*-Methylbenzophenone | i | (326) |
| N-Methylcaprolactam | i | (327) |
| 1-Methylcycloheptene | l(H$_2$) | (37) |
| 1-Methylcyclohexene | l(H$_2$) | (37) |
| 1-Methylcyclopentene | l(H$_2$) | (37) |
| Methylenecycloheptane | l(H$_2$) | (37) |
| Methylenecyclohexane | l(H$_2$) | (37) |
| Methylenecyclopentane | l(H$_2$) | (37) |
| Methylhydroxylamines | c | (397) |
| Methyl methacrylate | e | (398) |
| Methyl methacrylate—styrene | l(polym.) | (64) |
| Methyl methacrylate—vinylacetate | l(polym.) | (64) |
| Methylnaphthalenes($\alpha$ and $\beta$) | cd | (318) |

TABLE II (*continued*)

| Substance | Property | Reference |
|---|---|---|
| Methyl nitrite | jk | (399) |
| 4-Methylpentene-2 | l($H_2$) | (38) |
| N-Methylpiperidine | i | (327) |
| 2-Methylpropane-1-thiol | bcefhijklm(isom.) | (328, 400) |
| 2-Methylpropane-2-thiol | cijl(isom.) | (328) |
| Methylpropene | l(HCl, $SO_2$)n(HCl) | (332, 401) |
| N-Methylpyrrolidone | i | (327) |
| Methylsilane | c | (402) |
| α-Methylstyrene | lmn(polym.) | (403) |
| 3-Methyl-2-thiobutane | cijl(isom.) | (328) |
| *p*-Methylthiobenzoic acid | q | (371) |
| Myristic acid | cq | (352, 390) |
| Naphthalene | lmn($H_2$) | (404) |
| Neodymium ethyl sulfate | ef | (405) |
| Neopentyl bromide | f | (331) |
| Nicotinic acid | q | (387) |
| Nitrobenzene | q | (406) |
| Nitroethane | ij | (355) |
| Nitromethane | ij | (355) |
| 1-Nitropropane | ij | (355) |
| 2-Nitropropane | ij | (355) |
| Nitrotoluenes(*o*, *m*, *p*) | q | (406) |
| Nylon | i | (407) |
| Pentachlorophenol | efhijk | (353, 381) |
| Pentamethylene formal | il(polym.) | (351) |
| Perfluoro-*n*-butane | acd | (408) |
| Perfluoro-3-butyltetrahydrofuran | e | (409) |
| Perfluorobutyric acid | q | (410) |
| Perfluorodimethylcyclohexane | e | (409) |
| Perfluoroheptane | e | (409) |
| Perfluorohexane | abc | (410a) |
| Perfluoromethylcyclohexane | e | (409) |
| Phenol | cn(CO, $COCl_2$) | (343, 362) |
| Phosgene | fn(phenol) | (411) |
| Picolines(α, β, γ) | ac | (320) |
| Picolinic acid | q | (387) |
| Polyamides | b | (412) |
| Poly(ε-caprolactam) | i | (407) |
| Poly(1,1-dichloroethylene) | ij | (353) |
| Poly(ε-enanthrolactam) | i | (407) |
| Polyesters | b | (412) |
| Polyethylene | be | (413, 414) |
| Poly(ethylene sebacate) | e | (415) |
| Poly(methyl methacrylate) | e | (398) |
| Polystyrene | e | (398) |

TABLE II (*continued*)

| Substance | Property | Reference |
|---|---|---|
| Poly(trifluorovinyl chloride) | e | (409) |
| Polyvinylacetonyl ketone | mq | (416) |
| Poly(vinyl chloride) | ij | (353) |
| Propane | a | (337) |
| Propene | almn(HCl) | (337, 417) |
| Propionic acid | l(ioniz.)q | (56, 307) |
| Propiophenone | i | (311) |
| Propylamine | cd | (318) |
| n-Propyl nitrate | c | (389) |
| *n*-Propylphenylketone | i | (311) |
| *n*-Propyl thiolacetate | l($H_2O$) | (54) |
| Pyridine | ac | (320) |
| Pseudocumene | cd | (318) |
| Pyrrole | cd | (318) |
| Quinoline | cd | (318) |
| 8-Quinolinol-5-sulfonic acid and derivatives | q | (418) |
| Resorcinol | l($H_2SO_4$) | (419) |
| Sarcosine | q | (359) |
| 1,1,2,2,-tetrachloro-1,2-difluoroethane | e | (409) |
| Tetrachlorotetramethyl ammonium iodide | o | (150) |
| Tetracyclo(2:2:1:0:1)decadiene-2,7 | i | (327) |
| Tetraethyl tin | ij | (420) |
| Tetrafluorodinitroethane | ac | (421) |
| Tetrahydro-3,7-dimethyl-*s*-triazol(a)-*s*-triazol-1,5-dithine | ij | (306) |
| Tetrahydrofuran | ci | (349) |
| Tetrahydropyran | ci | (349) |
| Tetralin | lmn(dissoc.) | (404) |
| Tetramethylene formal | il(polym.) | (351) |
| 3,3,5,5-Tetramethylheptane | i | (327) |
| 4,4,6,6-Tetramethylnonane | i | (327) |
| 2,2,4,4-Tetramethylpentane | i | (327) |
| Tetramethyl tin | ij | (420) |
| 5,5,7,7-Tetramethylundecane | i | (327) |
| 2-Thiapentane | cij | (328) |
| 3-Thiapentane | cij | (328) |
| Thiosemicarbazide | ij | (306) |
| Titanium amyloxide | c | (422) |
| Titanium *t*-butoxide | c | (422) |
| Toluene | ac | (320) |
| Toluidines(*o*, *m*, *p*) | cd | (318) |
| *m*-Tolyl acetate | l($H_2O$) | (52) |
| Trifluorochloromethane | m($AlCl_3$) | (336) |
| Trihydroxyglutaric acid | q | (423, 424) |

TABLE II (*continued*)

| Substance | Property | Reference |
|---|---|---|
| Trimethylene formal | il(polym.) | (351) |
| 2,4,4-Trimethylpentene-1 | $l(H_2)$ | (38) |
| 2,4,4-Trimethylpentene-2 | $l(H_2)$ | (38) |
| Trimethylphosphine | ij | (425) |
| Triphenylchloromethane | $m(CH_3NO_2)q$ | (426) |
| Tropolone | q | (427) |
| L-Tyrosine | q | (428) |
| L-Valine | i | (379) |
| Vinyl acetate | l(polym.) | (63, 429) |
| Vinyl acetate—styrene | l(polym.) | (64) |
| Vinyl chloride | l(polym.) | (353) |
| Xylenes(*o*, *m*, *p*) | acd | (318, 320) |
| Xylenols | cd | (318) |
| D-Xylose | ln(isom.) | (12) |

TABLE III

GROUPS OF ORGANIC COMPOUNDS

| Substance | Property | Reference |
|---|---|---|
| 20 Acetophenones | q | (430) |
| Acetylation of cotton | l | (431) |
| 56 Aromatic acids | q | (432) |
| 40 Aromatic carboxylic acids | m(diphen. guanidine) | (433) |
| 31 Aromatic hydrocarbons | m(HF) | (266, 267) |
| 4 Aryloxyacetic acids | q | (434) |
| 9 Benzoic acids | q | (325) |
| 10 Benzylidenepyruvic acids | q | (325) |
| 3 Coumarins | q | (435) |
| Dimethylphenols | q | (436) |
| 6 Glycine dipeptides | q | (437) |
| 13 Hydrocarbons (high molec. wght.) | a | (438) |
| 12 Hydroquinones | q | (383) |
| Iodobenzene dichloride and 8 derivs. | m(dissoc.) | (439) |
| 12 Ketone cyanohydrins | m(dissoc.) | (440) |
| 6 Lutidines | ij | (441) |
| 8 Methylpyrrole carboxylic acids | q | (442) |
| 7 Nitroguanidines and related compounds | q | (443) |
| Olefins | $ln(SO_2polym.)$ | (444) |
| 69 Organic solids | c | (445) |
| 11 Terpene acids | q | (446) |
| Trimethylphenols | q | (436) |
| 11 Triterpene ketone cyanohydrins | m(dissoc.) | (447) |

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# EXPERIMENTAL MOLECULAR STRUCTURE[1]

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## Introduction

The appearance of the book *Tables of Interatomic Distances and Configuration in Molecules and Ions* by Sutton *et al.* (1) is a great event for all investigators in the field of molecular structure. The embryo of this collection of structure data was the compilation of results from gas electron-diffraction work by Allen & Sutton (2). This 27-page collection of structure data has been in daily use for nine years in many laboratories all over the world. No doubt the present collection will achieve an even greater distribution. It is incomparably larger in volume than the first collection (386 pages), and the inclusion of results from the whole field of experimental molecular structure increases its value enormously. Now, with the overwhelmingly large world literature on structural chemistry, the shorthand description that tables represent is very practicable. For this formidable work, Sutton has been fortunate in selecting a team of co-workers who rank among the foremost specialists in the field. The tables cover the literature to the end of the year 1955. A second volume covering the literature up to 1959 is announced, and it is hoped that it will appear without delay. On behalf of the workers in the field of molecular structure, the present authors wish to congratulate Sutton and co-workers on the successful result of their endeavors.

This collection of structure parameters and the anticipation of the next volume support the arguments of previous authors of the experimental molecular structure chapter for avoiding encyclopedic coverage. The choice of examples is delegated to the authors, and their subjective feeling of what is important and interesting may have been the guide to a certain extent, to their selection of material for the chapter.

Rather drastic omissions have been made for purely practical reasons. For instance, a substantial part of the x-ray crystallographic work has been omitted, in spite of its great importance for the field of experimental structural chemistry. This is partly a result of the complexity of many of these structures which would demand comprehensive use of spacious figures, and partly because a large fraction of the work is published in the universally available *Acta Crystallographica*. Inevitably, regional interests have also influenced the choice of subjects.

After some hesitation it was decided to exclude a discussion on force

[1] The survey of literature was completed in November, 1958.

constants and distance displacements as calculated from spectroscopic data and electron-diffraction experiments.

## Precision Measurements of Molecular Structure Parameters

The introduction of new methods, as well as further development of older methods, has considerably increased the accuracy of molecular dimension determinations. These measurements are limited, so far, to rather simple molecules. Many authors claim a reproducibility of principal bond distances in simple molecules from 0.005 A to 0.001 A or even better. Unfortunately, reproducibility and absolute accuracy can be of different orders of magnitude. Each of two investigators, studying the same compound, for instance, may be able to reproduce a distance (by successive repetitions of the measurement) with a standard deviation less than 0.001 A, but may obtain mean values differing by as much as 0.005 A or more. Even two investigators utilizing the same method principally may get results deviating appreciably more than the reproducibility each obtains.

As pointed out by several investigators, and as discussed in some detail by Bartell (3), the term "internuclear distance" today needs careful specification as to the method applied and the corrections made. This need will be more urgent with improvements in experimental methods. To bring various investigators using the same method to the same distance scale, it may be worth while to choose two or three reference compounds and try to agree upon some reference distances. Similar agreement may well be achieved among investigators applying different methods.

This is being done to a certain extent. A good example is the reinvestigation of the structure parameters of ethylene recently performed by three different high-precision methods. Apparently this is not a result of previous agreement, however, but more a fortunate coincidence caused by a long-felt need for more accurate data on this important compound. The most frequently quoted structural parameters for ethylene are those derived from a high-resolution infrared study of Gallaway & Barker (4) who reported the values 1.07 A, 1.353 A, and 119.9° for the C—H bond, the C=C bond, and the H—C—H angle, respectively. Recent studies of substituted ethylenes suggest a somewhat shorter C=C bond distance. The first of the three new investigations of ethylene was carried out by Bartell & Bonham (5), applying the modern rotating-sector electron-diffraction method. A distinction was made between the distances obtained from the positions of the maxima of the radial distribution curve ($r_m$) and those obtained from the centers of gravity of the peaks of the probability-distribution curve ($r_g$). The reported H—C—H angle was calculated from the $r_g$ values. The investigation must be considered as preliminary. Refinements based upon least-squares calculations are announced. The second of the new investigations was carried out by Allen & Plyler (6) using a high-resolution infrared spectrometer. A combined study of $C_2H_4$ and $C_2D_4$ gave sufficient information for the determination of the three structure parameters. The third study on ethylene was

carried out by Dowling & Stoicheff (7), applying high-resolution Raman spectroscopy (8). The analysis of about 120 lines in the $C_2H_4$ spectrum and about 100 lines in the $C_2D_4$ spectrum led to a highly accurate determination for both molecules of the large moments of inertia and the small moments of inertia. These moments of inertia are given as average values for the state $v=0$. This means that the derived structure parameters are not equilibrium-state values but suffer from the effect of zero point vibration. The results of the three different studies are summarized in Table I. The agreement is very satisfactory; it demonstrates that the earlier accepted values were not correct. Analogous simultaneous attacks on important molecules by different methods is to be desired.

TABLE I

STRUCTURE PARAMETERS FOR ETHYLENE

| | Electron diffraction Bartell & Bonham (5) | | Infrared Allen & Plyler (6) | Raman Dowling & Stoicheff (7) |
|---|---|---|---|---|
| | $r_m$ | $r_g$ | | |
| C—H | 1.074 ± 0.005 A | 1.085 A | 1.086 ± 0.003 A | 1.086 ± 0.003 A |
| C=C | 1.330 ± 0.003 A | 1.334 A | 1.337 ± 0.003 A | 1.339 ± 0.002 A |
| H—C—H | | 116° | 117.37° ± 1° | 117.57° ± 0.5° |

The short C=C bond distance of ethylene could now advantageously be compared with C=C bonds in more complicated molecules. Electron-diffraction studies on cyclo-octatetraene (9), 1,3-butadiene (72), and vinylacetylene (10) led to a C=C distance of 1.334, 1.337, and 1.336 A, respectively. This demonstrates that the double bond in conjugated systems is not lengthened detectably because of resonance, while the C—C single bond is appreciably affected.

A microwave study carried out by Bak *et al.* (12) gave as the result a C=C distance for vinyl fluoride of 1.333 A. These and other examples seem to support a general rule that the lengths of carbon—carbon bonds are dependent on the type of adjacent bonds rather than the type of adjacent atoms. This view has been put forth in the last few years by various investigators in the field of structure chemistry. It has been explicitly advocated by Stoicheff (8) who categorizes the various kinds of carbon—carbon bonds according to the adjacent bonds. (The ethylene C=C distance of 1.344 A chosen by Stoicheff was a trifle too large according to the latest measurements.)

If the C=C double bond is neighbored by other double bonds a shorter distance value is found. High-resolution Raman spectroscopic studies carried out by Stoicheff (13) led to a C=C bond distance of 1.309 A for allene. Practically the same value is found from electron-diffraction studies (14).

Stoicheff found the distance 1.284 A for the central C=C bond in butatriene, a value that should be compared with the two C=C bond-distance values of 1.279 A (10) and 1.28 A (11) in carbon suboxide found by electron-diffraction studies.

Of course, the general rule mentioned above must not be considered free of exceptions. For instance, a molecule such as cyclopropene, may be expected to be an exception to the rule because of the unusual valency-angle conditions, as is cyclopropane (15). In fact, a microwave study by Kasai *et al.* (16) led to a C=C bond distance for cyclopropene of 1.300 A, i.e., a considerably lower value than that of ethylene.

According to the bond-length rule, the carbon—carbon triple bond distance should have one single value in all compounds. This view is supported by microwave studies (17–21) covering six various acetylene derivatives. With one exception, the C≡C bond distance is found to be close to the value of 1.207 A, which is the value chosen by Stoicheff in his list (8). This is in excellent agreement with recent microwave data (38) and with electron-diffraction data for dimethyldiacetylene (22) and vinylacetylene (10) which are 1.208 A and 1.205 A, respectively.

Further experimental studies in this field, supported by theoretical considerations, would be of great value. Increasing accuracy in structure determination might lead to the development of a general quantitative law for the classification of internuclear distances. This would be of great help in predicting the structure of more complicated molecules.

Because of the extremely high accuracy obtainable, the microwave method is of particular value for precision determination of molecular parameters. In spite of the well-known limitation of the method, the microwave spectra of a great number of substances are being studied. For theoretical reasons the heteronuclear diatomic molecules are particularly well suited to microwave spectroscopic studies. Unfortunately, the number of diatomic molecules which can be studied at room temperature are severely limited by the small fraction of such substances with sufficient vapor pressure. However, the development of the high-temperature spectrometer (23, 24) has made it possible to observe the pure rotation spectra of most of the alkali halides (25). This technique has further been applied in a recent work of Barrett & Mandel (26) who have studied the microwave spectra of Tl, In, and Ga monohalides (with the exception of InF and GaF). The microwave spectra were obtained using the spectrometer of Townes at Columbia University and a wave guide which can be heated to a temperature of 1000°C. The obtained internuclear equilibrium distances are given in Table II. The distances refer to $^{205}$Tl, $^{115}$In, $^{69}$Ga, $^{35}$Cl, $^{79}$Br, and $^{127}$I. Except for InI, the given error range is $\pm 0.0001$ A; for InI it is $\pm 0.0009$ A. Because of the high accuracy, members of these series might be used as standard substances for other methods. In the case of the electron-diffraction method, the phase shift effect resulting from the difference in atomic number (27) might cause difficulties. On the other hand, the molecules might be well suited to a study of

TABLE II

THE INTERNUCLEAR EQUILIBRIUM DISTANCES FOR TL, IN, AND GA MONOHALIDES OBTAINED BY MICROWAVE STUDIES (26)

| | F | Cl | Br | I |
|---|---|---|---|---|
| Tl | 2.0844 A | 2.4848 A | 2.6181 A | 2.8135 A |
| In | | 2.4011 A | 2.5432 A | 2.7539 A |
| Ga | | 2.2017 A | 2.3525 A | 2.5747 A |

the phase shift effect. Barrett and Mandel point out a possible source of error in electron-diffraction studies of metal monohalides, namely, the tendency of dimerization of the vapor or the formation of trihalides in the case of Tl. This would not affect the spectroscopic results but would make the electron-diffraction values larger. However, the electron-diffraction work on the metal monohalides is rather old (28, 29), and the results deviate appreciably from the microwave data. The electron-diffraction studies therefore should be repeated.

As the number of structure parameters increases, the amount of work necessary for a complete microwave structure analysis is drastically augmented. The complete determination of the structure of pyridine carried out by Bak *et al.* (30, 31) may serve as a good example of a successful attack on a many-parameter problem. With the trivial assumption of planarity and a plane of symmetry perpendicular to the ring plane, ten parameters have to be determined. Isotopic mixtures of ordinary pyridine with 2-$^{13}$C- and with 3-$^{13}$C-pyridine were studied. Combining this with the results found from the microwave spectra of 2D-, 3D-, and 4D-pyridine gave a total of eleven relations between the ten geometric parameters. The parameters calculated from these relations are given in Table III. The distances were determined with an accuracy of $\pm 0.001$ A. It is interesting to note that the two different types of C—C bond distances in the pyridine ring are found to be the same within the error of the method, namely, 1.3945 A. As far as present structure parameter methods can tell, this value is equal to the value of 1.397 A obtained

TABLE III

THE STRUCTURE PARAMETERS OF PYRIDINE (31)

| Distances | | Angles | |
|---|---|---|---|
| $N—C_2$ | 1.3402 A | $C_6—N—C_2$ | 116.83° |
| $C_2—C_3$ | 1.3945 A | $N—C_2—C_3$ | 123.88° |
| $C_3—C_4$ | 1.3944 A | $N—C_3—H_3$ | 115.88° |
| $C_2—H_2$ | 1.0843 A | $C_4—C_3—H_3$ | 121.30° |
| $C_3—H_3$ | 1.0805 A | | |
| $C_4—H_4$ | 1.0773 A | | |

for the C—C bond distance in benzene (32, 33, 34). This is in contrast to the results of resonance considerations. According to the usual considerations, the resonance hybrid of pyridine should consist of two Kekule structures of equal weight, three Dewar structures of equal weight, two $\alpha$-ionic structures of equal weight, and one $\gamma$-ionic structure. The presence of the last structure has led to the prediction that the $C_3$—$C_4$ bond distance should be slightly longer than the $C_2$—$C_3$ distance. The fact that the two bond distances are found to be the same and equal to the C—C bond distance of benzene is in accord with the general concept of bond distances discussed above.

Friend & Dailey (15) have studied the structure of cyclopropyl chloride and cyclopropyl cyanide, using microwave spectroscopy. The rotational constants for five molecular species were studied, namely, two chlorides ($^{35}Cl$ and $^{37}Cl$), the *cis* and *trans* 2-substituted deuterated cyanides, and the normal cyanide. The distances reported are: C—C in ring, 1.5131 A; C—Cl, 1.7780 A; C—C(CN), 1.4679 A; C≡N, 1.1574 A; C—H for the chloride, 1.105 A; and C—H for the cyanide 1.112 A. The H—C—H angle reported for the chloride is 114.60° and for the cyanide, 115.58°. The values given for the angles H—C—Cl and H—C—C(CN) are 120.88° and 119.58°, respectively.

A microwave study by Hirota, Oka & Morino (35) on propargyl chloride led to a C—Cl bond distance of 1.7802 A. This value is based upon an assumed C≡C bond distance of 1.207 A. The result differs from the electron-diffraction value of $1.82 \pm 0.02$ A reported by Pauling *et al.* (36).

Most precision determinations of structure parameters using the microwave method are based upon the study of a set of isotopic substituted species. The influence of the substitution on bond lengths and valency angles is studied by Laurie (37) and Costain (38). Although the effect does not seem to be very large it should be carefully accounted for in every case.

## Internal Rotation

The restriction on the internal rotation about single bonds is of great importance for our understanding of the structure of free molecules. The work in this field has been concentrated, first of all, on such simple molecules as ethane derivatives; but studies on rotational isomerism and potential barriers might also throw light on our understanding of macro-molecules, such as proteins and other polymers.

The experimental data on internal rotation were reviewed by Mizushima and Shimanouchi in the *Annual Review of Physical Chemistry* of 1956 and in Mizushima's book covering the literature up to 1953 (39). Further, the spectroscopic results in the field were reviewed by Wilson and Crawford in the *Annual Review of Physical Chemistry* of 1958.

Various experimental methods are used to derive values for energy differences of rotational isomers and potential barriers. The methods most frequently used are based upon microwave spectroscopy, electron diffraction, and thermodynamic measurements.

The molecular structure and the rotational isomerism of n-propyl chloride have been studied by Morino & Kuchitsu (40) using the electron-diffraction sector method. It was found to be an equilibrium mixture of the *trans* and *gauche* forms. The azimuthal angle of the *gauche* form was found to be $59° \pm 5°$ in contrast to the value of approximately 70° found for molecules like 1,2-dichloroethane (41). The fraction of the *trans* form was found to be $19 \pm 5$ per cent. Keeping in mind the fact that the statistical weight of the *gauche* isomer is two, it can be shown that the *gauche* form is more stable than the *trans* form by a few hundred calories per mole. This is in fair agreement with spectroscopic data (42) but significantly smaller than the value obtained for 1,2-dichloroethane of 1100 cal./mole (43).

Morino & Hirota (44) have studied the molecular structure and internal rotation of hexachloroethane, hexachlorodisilane, and trichloromethyltrichlorosilane, using the electron-diffraction method. In this case, particular interest was taken in the height of the potential barriers. The values obtained are 10.8, 4.3, and 1 kcal./mole for $C_2Cl_6$, $SiCCl_6$, and $Si_2Cl_6$, respectively. The uncertainty in the two first numbers was estimated to be 3 and 0.8 kcal./mole, respectively. In the case of hexachlorodisilane it is claimed that the barrier height is positively different from zero, in accordance with the result of Swick & Karle (45).

An interesting example of a molecule of a somewhat different kind is the sulphur monochloride, $S_2Cl_2$, studied by Hirota (46). He found a dihedral angle between the two S—S—Cl planes of 82.5° from the *cis* position, and a hindering barrier of about 17 kcal./mole.

In the last few years, methods have been developed which allow the determination of potential barriers from microwave spectra with a rather high degree of accuracy. The method which seems to have found greatest use in practice was developed at Harvard University by Wilson and co-workers (47 to 56). They have focused their interest primarily upon molecules containing a methyl group as the main rotating unit. The methyl group is treated as a rigid symmetric top attached to a rigid framework. If the internal torsional rotation is separated from the over-all rotation of the molecule, the wave equation for the internal rotation can be studied easily. As a first approximation, a potentional energy of the form

$$V(\alpha) = \tfrac{1}{2}V_3(1 - \cos 3\alpha)$$

is assumed, where $\alpha$ is the angle of internal rotation. By this approximation the wave equation will be a special case of the Mathieu differential equation. For very high barriers the lower torsional energy levels are similar to those of a harmonic oscillator, except in that they are triply degenerate because of the existence of the three equivalent potential wells. At lower barriers the levels are split into a nondegenerate level and a doubly degenerate level as a result of the "tunnel effect." The splitting is a sensitive function of the barrier height, $V_3$, and the reduced moment of inertia of the molecule as a whole. The angular momenta for internal and over-all rotation are coupled,

and the extent of the coupling differs for the two sublevels. The torsional state does not change during a rotational transition. The coupling, therefore, leads to a doublet splitting; and the microwave spectrum consists of doublets instead of single lines, as would be expected for a rigid molecule. The coupling and, thus, the magnitude of the doublet separations is a function of the product of the barrier height and the reduced moment of the molecule. If the reduced moment is known from structure parameter determinations, the barrier height can accordingly be deduced from the measurements of the doublet separations.

A list of potential barriers and equilibrium orientations has been published by Wilson (51). According to private information from Wilson, the barrier values are believed to be accurate to $\pm 5$ per cent except for two cases, namely for methyl mercaptan and methyl germane. A recent study of Kojima & Nishikawa (57) on methyl mercaptan has shown that the barrier value is $1269 \pm 28$ cal./mole, rather than 710 cal./mole as given in Wilson's table. Further, unpublished measurements of Laurie (58) lead to a potential barrier of $1239 \pm 35$ cal./mole for methyl germane instead of the minimum value of 2500 cal./mole reported by Wilson.

In a series of interesting papers by Lide & Mann (59 to 63), also based upon the microwave spectra, the internal rotation has been studied for molecules containing not only one but three methyl groups. In the first two of these papers, propylene (59) and methylallene (60) have been studied. For propylene the internal potential barrier is found to be $1978 \pm 17$ cal./mole in good agreement with the value of 1950 cal./mole obtained previously from calorimetric measurements (64). For methylallene the potential barrier is found to be $1589 \pm 6$ cal./mole. The value obtained from calorimetric measurements is 1650 cal./mole (65). In the case of trimethylamine (61) the situation is a little more complicated as the three methyl groups can not be presumed independent. However, the analysis of the microwave data shows that the potential experienced by one given group does not depend very much on the orientation of the other two groups. A value of 4400 cal./mole may, to within an accuracy of 10 or 20 per cent, be compared with the usual barrier heights determined for simple molecules with a single internal rotational degree of freedom. Again, this value might be compared with the one-dimensional barrier of 4270 cal./mole per methyl group found by Aston *et al.* (66) from heat-capacity measurements. For the three molecules, isobutane, tertiary butyl fluoride, and trimethylphosphine (62), it is also found that the potential barrier of one methyl group does not seem to be greatly influenced by the orientation of the other methyl groups in the molecule. The barrier values for the three compounds isobutane, tertiary butyl fluoride, and trimethylphosphine are found to be 3900, 4300, and 2600 cal./mole per methyl group, respectively. The value for isobutane is in good agreement with the two reported thermodynamic values, 3620 (67) and 3870 cal./mole (68). Finally ethyl chloride and ethyl bromide (63). were

studied, leading to potential barrier values of $3560 \pm 12$ and $3567 \pm 20$ cal./mole, respectively.

A series of potential barrier values which are either not given in the list by Wilson (51), mentioned earlier, or have been revised since that list was published are given in Table IV.

Of considerable theoretical interest is the question of a possible restriction on the freedom of rotation in molecules like dimethylacetylene and derivatives. Electron-diffraction studies on 1,4-dichlorobutyne-2 (69) and

TABLE IV

INTERNAL ROTATIONAL BARRIERS FOR A SERIES OF MOLECULES CONTAINING METHYL GROUPS

| Molecule | Microwave data | Thermodynamic data |
|---|---|---|
| $CH_3—CH=CH_2$ | $1978 \pm 17$ cal./mole (59) | 1950 cal./mole (64) |
| $CH_3—CH=C=CH_2$ | $1589 \pm 6$ cal./mole (60) | 1650 cal./mole (65) |
| $(CH_3)_3N$ | 4400 cal./mole (61) | 4270 cal./mole (66) |
| $(CH_3)_3CH$ | 3900 cal./mole (62) | 3620 cal./mole (67)<br>3870 cal./mole (68) |
| $(CH_3)_3CF$ | 4300 cal./mole (62) | |
| $(CH_3)_3P$ | 2600 cal./mole (62) | |
| $CH_3—CH_2Cl$ | $3560 \pm 12$ cal./mole (63) | |
| $CH_3—CH_2Br$ | $3567 \pm 20$ cal./mole (63) | |
| $CH_3SH$ | $1269 \pm 28$ cal./mole (57) | |
| $CH_3GeH_3$ | $1239 \pm 25$ cal./mole (58) | |

the corresponding bromocompound (70) are in accordance with free rotation. On the other hand, the electron-diffraction studies cannot exclude a smaller potential barrier of say 100–200 cal./mole. It can, however, exclude a high potential barrier of the order of magnitude of that of ethane and its derivatives. This result is in good agreement with estimates made by Morino and collaborators (71). They found a constant dipole moment for the 1,4-dichlorobutyne-2 in the temperature range from 90–160° C., from which they concluded that the barrier height is less than 100 cal./mole. According to the information available to the present authors, no experimental evidence has been produced for a finite potential barrier in this kind of molecules. Because of the fundamental importance of the problem, further experimental efforts should be made in order to throw more light on the problems.

Several times in the past the question of a possible internal rotation in the 1,3-butadiene molecule has been discussed. A recent electron-diffraction study (72) seems to demonstrate that a rather rigid *trans* form is the only dominating conformation at normal temperatures.

A new experimental approach to the study of rotational isomerism is

based upon the measurements of dispersion of sound velocity in liquids. Measurements of this kind were carried out on ethyl formate by Tabuchi (73). From these experiments the energy differences, the equilibrium constants, the rate of isomerization, and the height of the potential barrier hindering the internal rotation about the C—O bond were studied. The *cis* and *trans* forms were assumed to represent the two stable conformations with an energy difference of 2.5 kcal./mole. The height of the potential barrier as calculated from the higher energy state was found to be 3.38 kcal./mole.

## Addition Compounds

In a series of papers over the last few years, Hassel & his co-workers (74 to 80) describe structures of so-called addition compounds which have been studied crystallographically in the solid state. This is a field which shows the existence of molecular connections intermediate between normal covalent bonds and ordinary van der Waals contacts, thereby demonstrating the somewhat arbitrary character of the ordinary concept of a molecule. The compounds are not likely to be included in general compilations of molecular structures and bond distances, and, therefore, they are reviewed at some length.

The molecular addition complexes studied by Hassel are mainly of the kind which is formed between ethers, ketones, or amines, on the one hand, and halogens or interhalogen compounds, on the other. The short distance between the partners in a complex, in all cases, is between an oxygen or a nitrogen atom and a halogen atom. The compounds are often unstable as solids at ordinary temperature, but are formed by moderate cooling. The studies are made by x-rays on single crystals grown in capillary tubes and maintained at low temperature during exposure.

Analogous complexes formed in solution have been studied spectroscopically by Mulliken & Reid (81, 82) and have been described as charge transfer complexes. Following an idea of Benesi & Hildebrand (83), the complexes are now generally assumed to be formed by a Lewis acid-base interaction, oxygen atoms in ethers and ketones, and nitrogen atoms in amines acting as electron donors (the acceptor being a halogen atom). The suggestions as to the geometry of the complexes in solution given by Mulliken from theoretical considerations are, not, however, in accord with the structures found by Hassel in the solid state.

The main feature found in the structures of these complexes in the solid state is the prevalent collinear arrangement of the oxygen, or the nitrogen atom and the two atoms of the halogen or interhalogen molecule. Further, the oxygen-halogen and nitrogen-halogen distances are considerably shorter than the respective sums of van der Waals' radii, indicating the presence of an intermediate kind of bond. In the cases of a complex between an amine and iodine or iodine monochloride, the nitrogen-iodine distance is only 12 to 13 per cent longer than the sum of covalent radii, showing a very strong

interaction. On the other hand, a lengthening of the halogen-halogen distance relative to the bond length in the free halogen molecule indicates a weakening of this bond as a result of a change in electronic structure. It is of interest also to point out that in the cases in which an interhalogen molecule (such as iodine monochloride) takes part in the formation of an addition complex, the iodine atom is the one which is linked to the electron donor, indicating that the acceptor function of iodine is stronger than that of chlorine.

Table V gives a list of interatomic distances in a selection of complexes reported to date. As expected, the differences between the observed interatomic distances and normal covalent bond lengths, or van der Waals' distances are

TABLE V

INTERATOMIC DISTANCES IN ADDITION COMPOUNDS STUDIED BY HASSEL *ET. AL.*

| | Bond | Length obs. (A) | Sum of covalent radii | Bond | Length obs. (A) | Sum of covalent radii | Sum of van der Waals' radii |
|---|---|---|---|---|---|---|---|
| 1,4-Dioxane-$Br_2$ | Br—Br | 2.31 | 2.28 | O—Br | 2.71 | 1.80 | 3.35 (74) |
| Acetone-$Br_2$ | Br—Br | 2.28 | 2.28 | O—Br | 2.82 | 1.80 | 3.35 (79) |
| Hexamethylene-tetramine-2 $Br_2$ | Br—Br | 2.43 | 2.28 | N—Br | 2.16 | 1.84 | 3.45 (74a) |
| Trimethylamine-ICl | I—Cl | 2.53 | 2.32 | N—I | 2.30 | 2.03 | 3.65 (77) |
| Trimethylamine-$I_2$ | I—I | 2.84 | 2.66 | N—I | 2.27 | 2.03 | 3.65 (77) |
| Pyridine-ICl | I—Cl | 2.54 | 2.32 | N—I | 2.30 | 2.03 | 3.65 (75, 76) |

more pronounced in the cases where nitrogen acts as electron donor. Another difference between ethers or ketones on the one hand and amines on the other is that complexes formed with the former in the solid state occur in endless chains with halogen molecules acting as bridges between two ether or ketone molecules. In contrast to this, amine-halogen addition compounds occur as isolated 1:1 complexes, a situation which is probably similar to that in solution.

The angles which the intermediate kind of bond makes with the ordinary covalent bonds in the donor molecule are also worth mentioning. In complexes formed by an ether or tertiary amine, the angle between an O—C, or an N—C bond and the oxygen-halogen, or a nitrogen-halogen direction is close to the tetrahedral angle. In the case of a ketone, i.e., in the acetone-bromine complex, the oxygen atom is attached to two halogen atoms belonging to two different halogen molecules (79), the two O—Br—Br lines form an angle of 110° at the oxygen atom. The plane formed by these two directions makes a small angle (16°) with the C—C—C plane of the acetone molecule. This is probably due to the attainment of favorable van der Waals' distances between methyl groups and the nearest halogen atoms.

Complexes of a somewhat different kind are those in which benzene acts as a Lewis base. Hassel & Strømme have studied a solid 1:1 compound be-

tween benzene and bromine (80). They find a bromine-bromine distance very close to that observed in the free molecule. The line joining the two bromine atoms passes through the midpoint of the benzene ring, and makes an angle with the benzene plane which at least is very nearly 90°. The distance found from a bromine atom to the benzene plane is 3.36 A, which in comparison to a normal packing distance of about 3.80 A, shows that an intermediate kind of bond is present. Both halogen atoms of one molecule are joined equally to benzene molecules, with the result that endless chains of alternating bromine and benzene molecules exist in the solid state.

A complex of another kind in which benzene acts as electron donor can be formed between benzene and silver perchlorate. The gross features of its structure have been known for some years (84), but a refinement revealing new details has been reported recently by Smith & Rundle (85). In this complex, also, chains of alternating benzene molecules and silver ions occur. The silver ions are not situated on the axis of the benzene ring, but the two silver ions associated with each benzene molecules lie above and below opposite bonds of the benzene ring. The planes of two benzene molecules associated with one silver ion are not parallel. Although the attachment of a silver ion of the two benzene rings is identical, the position of the silver ion with respect to the two carbon atoms of the bond is asymmetric and disordered (the silver-carbon distances being 2.50 and 2.63 A). A further peculiarity is the reported distortion of the benzene ring with two C—C distances equal to 1.35 A, and four equal to 1.43 A.

Another very interesting complex reported to exist between a silver ion and an organic $\pi$-bonding system is one formed by silver nitrate and cyclo-octatetraene (86). Here the strongest interaction is between one silver ion and one cyclo-octatetraene molecule. The closest Ag—C distances are 2.5 A, which is not much greater than the sum (2.3 A) of covalent radii. The average distance of 1.37 for C=C gives plausibility for an increase of this distance as compared to that of the free molecule.

## Miscellaneous

Because of the unfortunate lack of knowledge of the Russian language, many contributions in the field of molecular structure are overlooked by scientists in the Western World. Parts of the important work of the group of Pinsker and Vainstein on electron diffraction on solids has been reviewed in English by Semiletov (87). A more detailed description of their method, including a historical outline and a series of structure examples, has recently been given by Pinsker & Vainstein themselves (88). Lashkarev & Usyskin (89) early applied the electron diffraction method for the localization of the hydrogen atom in crystals. Later this method was adopted by Pinsker & Vainstein and Lobatshev for the determination of hydrogen in paraffins (90, 91). Perhaps the most successful work along this line is the classical example of diketopiperazine (92) studied by Vainstein. A three-dimensional Fourier potential map gave well-resolved maxima for the hy-

drogen atoms. In a review article some recent data on the crystal chemistry of hydrogen compounds have been presented (93), including the latest data on the C—H, N—H, and O—H bond distances, as well as M—H distances in some metal hydrides. The distance from a hydrogen atom to another atom in the crystal was described by the following radii: ionic radius, 1.5 A; covalent radius, 0.30–0.35 A; and radius in metallic hydrides, 0.41 A. It was pointed out that there is a deviation from additivity for distances between hydrogen atoms and other atoms. The C—H distance in paraffins (94) was found to be 1.12 A, a value that is definitely larger than the C—H distance of benzene of 1.080 to 1.085 A (32, 34). It was also a trifle larger than the C—H bond generally observed for paraffins in gas molecules, as found, for instance, by Kuchitsu & Morino (95) to be $1.098 \pm 0.003$ A. The value is also significantly larger than the methyl *C*—H bond distance given by Stevenson & Ibers in their review article in the *Annual Review of Physical Chemistry* of 1958 (96) and the C—H distances listed by Cumper (97).

It is worth noting that the new scattering amplitudes for electron diffraction of Vainstein & Ibers were published in a recent issue of *Kristallografiya* (98). The impressive activity of the groups of Pinsker & Vainstein can perhaps best be demonstrated by summarizing a few compounds recently studied that are of particular interest for the structure of molecules: (*a*) nitrides of iron (100, 103), chromium (100), molybdenum (99, 100), and tungsten (100); (*b*) cubic modification of $(NH_4)_2GeF_6$ (101); (*c*) thallium selenide (102); and (*d*) cubic modification of $CuCl_2 \cdot 3\ Cu(OH)_2$ (104).

A series of high-temperature gas electron-diffraction studies has been performed by Akishin *et al.* (105 to 119) at Moscow State University. The molecules are primarily of the type $MX_2$, where M mainly represents atoms of the second-group metals and X represents halogen atoms. About 40 compounds of this kind have been studied. The electron-diffraction unit is specially designed for the study of low-volatile compounds. The particular difficulties which arise when studying compounds with boiling points over 1000°C. were overcome by the use of a specially constructed evaporator with an ampule inserted in it. The ampule is heated through electron bombardment. The photographic emulsion has to be protected against the light which is radiated from the hot parts of the evaporator. The method of visual inspection of the electron-diffraction pattern has been applied. A rotating sector has also been tried out in a special case, and photometer curves are being studied. The intensity data for this kind of molecules usually extend to $s$ equal to 15 to 25 $A^{-1}$. The structure determinations are based upon the studies of intensity curves and radial distribution curves. Within the error of the method, the molecules are found to be linear in accordance with the quantum chemical concept of directed valences. In most cases the XMX angle is determined to be 180° with an error range of approximately ±10°. In several cases the uncertainty is somewhat larger. The M—X bond distances are listed in Table VI. From these distances, new covalent radii of alkali-earth metals have been calculated following the additivity rule of

TABLE VI

INTERATOMIC DISTANCES IN THE HALOGENIDES OF THE SECOND GROUP ELEMENTS OBTAINED BY AKISHIN *ET AL.* (109)

| Elements | F | Cl | Br | I |
|---|---|---|---|---|
| Be | 1.40 ± 0.03 A (119) | 1.75 ± 0.02 A (119) | 1.91 ± 0.02 A (119) | 2.10 ± 0.02 A (119) |
| Mg | 1.77 ± 0.02 A (110) | 2.18 ± 0.02 A (110) | 2.34 ± 0.03 A (110) | 2.52 ± 0.03 A (117) |
| Ca | 2.10 ± 0.03 A (111) | 2.51 ± 0.03 A (111) | 2.67 ± 0.03 A (111) | 2.88 ± 0.03 A (111) |
| Sr | 2.20 ± 0.03 A (113) | 2.67 ± 0.03 A (113) | 2.82 ± 0.03 A (113) | 3.03 ± 0.03 A (113) |
| Ba | 2.32 ± 0.03 A (114) | 2.82 ± 0.03 A (114) | 2.99 ± 0.03 A (114) | 3.20 ± 0.03 A (114) |
| Zn | 1.81 ± 0.02 A (107) | 2.05 ± 0.01 A (105) | 2.21 ± 0.01 A (105) | 2.38 ± 0.02 A (105) |
| Cd | 1.97 ± 0.02 A (109) | 2.21 ± 0.02 A (106) | 2.37 ± 0.02 A (106) | 2.55 ± 0.02 A (106) |
| Hg | | 2.29 ± 0.02 A (109) | 2.41 ± 0.02 A (109) | 2.59 ± 0.05A(109) |

Schomaker & Stevenson (120). These radii are given in Table VII. It should also be mentioned that the group of molecules $PbX_2$ and $SnX_2$ for fluorine, chlorine, bromine, and iodine has been studied and new bond distances obtained (116).

In a recent work, Akishin *et al.* have studied lithium oxide in the gaseous state by electron diffraction (118). A molybedenum ampule was heated to a temperature of 1300–1350°C., and the time of exposure was from 15 sec. to 1.5 min. The Li—O distance was determined to 1.82 ± 0.015 A. The valency angle was difficult to deduce from the electron-diffraction data because of the dominating contribution of the Li—O distance as compared to the Li—Li distance. An angle of 110° was given as the most probable value.

Livingston *et al.* (121) have carried out electron-diffraction studies on vinylidene chloride using the visual method on nonsectored and sectored plates as well as the sector-microphotometer method. The C=C bond distance is found equal to 1.324 ± 0.020 A, a value compatible with the short distance found for ethylene (5, 6, 7). The other structure parameters obtained are: C—Cl, 1.710 ± 0.010 A, and for the Cl—C—Cl angle, 114.5° ± 1°.

Unfortunately only a few experimental studies on the Schomaker and Glauber effect in electron diffraction have reached the literature since the effect was announced (27). In a recent reinvestigation of lead tetramethyl, Wong & Schomaker (122) have shown the diffraction pattern to be in agree-

TABLE VII

COVALENT RADII FOR THE SECOND-GROUP ELEMENTS (109)

| Element | Covalent radius | Elements | Covalent radius |
|---|---|---|---|
| Be | 0.85 | Ba | 1.96 |
| Mg | 1.29 | Zn | 1.14 |
| Ca | 1.64 | Cd | 1.30 |
| Sr | 1.79 | Hg | 1.33 |

ment with a symmetrical molecular structure, and the complex atomic scattering factors of Ibers & Hoerni (123). The reported Pb—C distance is $2.203 \pm 0.010$ A. The H—C—Pb angle was found to be $109° \pm 4°$ if a C—H distance of 1.09 A was assumed. A reinvestigation of $CF_3I$ by the same authors also confirmed the scattering factors of Ibers and Hoerni.

The last year has brought a new example of the impressive achievements in the low temperature x-ray crystallographic studies on boron hydrides. With the determination of the molecular structure of $B_6H_{10}$ carried out by Hirschfeld *et al.*, the structure investigations of the presently well-characterized boron hydrides by Lipscomb & co-workers are declared to be completed (124). This last member is shown to possess an approximately pentagonal pyramidal arrangment of boron atoms. The hydrogen arrangement has the lower symmetry of a mirror plane. There are four bridge hydrogen atoms, each connecting a pair of boron atoms at the base of the pyramid. The fifth B—B link at the base has the unusually short length of 1.60 A. It seems possible now to classify the higher boron hydrides in two series, namely, $B_nH_{n+4}$ ($n = 5, 6, 10$) with no $BH_2$-groups, and the less stable series $B_nH_{n+6}$ ($n = 4, 5, 9$) with at least one $BH_2$-group.

With respect to boron halogenides, it is of interest to point out the short B—B distance found in $B_2F_4$ (125) of $1.67 \pm 0.04$ A, as compared with the B—B distance of $1.75 \pm 0.05$ A in $B_2Cl_4$. In connection with boron compounds it should be pointed out that the relatively unexplored field of substituted boranes has been opened by application of the nuclear magnetic resonance method of the substances $B_5H_8Br$, $B_5H_8I$, $B_{10}H_{13}Br$, $B_{10}H_{13}I$ (m.p. 116°), and $B_{10}H_{13}I$ (m.p. 72°) and the points of substitution have been conclusively determined (126).

In pursuance of studies on electron-deficient compounds, Amma & Rundle report a structure determination of trimethylindium (127). This structure shows several highly interesting details. Four molecules are connected by methyl bridges to a tetramer of symmetry $\bar{4}$. In contrast to the angular methyl bridges which occur in dimer trimethylaluminium and polymer dimethylberyllium, the bridges in tetramer trimethylindium are found to be linear with uneven In—C distances of 2.15 and 3.11 A.

New contributions have been made to the knowledge of the configurational environment of sulphur atoms in a wide range of compounds. The comprehensive x-ray crystallographic studies of Foss & co-workers on polythionic compounds (128 to 138) have recently been extended to a structure determination of a hexathionate ion. A general feature of the structure of polythionates and other polythionic compounds is the occurrence of unbranched and nonplanar sulphur chains. In polythionates three oxygen-atoms are bonded to each of the terminal sulphur atoms of the chain. Analogous and often isomorphous structures have been found in cases where the middle sulphur atom of a pentathionic compound has been replaced by selenium or tellurium. A structural detail which occurs whenever there is a sequence of atoms X—S—S—Y in an open chain is that the azimuthal

angle between the planes through X—S—S and S—S—Y lies in the range 80°–110°. Probably the simplest demonstration of this is found in the structures of sulphur monochloride and monobromide in the gaseous state, determined by Hirota by electron diffraction and previously referred to (46). An exception to an azimuthal angle in the mentioned range is to be expected in a cyclic disulphide. In the five-membered ring of two sulphur and three carbon atoms which occurs in 1,2-dithiolane-4-carboxylic acid, Foss & Tjomsland found an azimuthal angle of 20° (128).

The nonplanarity of the sulphur chains makes *cis-trans* isomerism possible in open chain compounds when the chain contains more than four members. In a chain of five, the terminal atoms may lie on the same side (*cis*) or on opposite sides (*trans*) of the plane through the three middle sulphur atoms. When there are six atoms in a chain, three forms should be possible, namely, *cis-cis*, *cis-trans*, and *trans-trans*. The *cis* form in the five-membered chain and the *cis-cis* form of the six-membered one represent segments of the $S_8$-ring in orthorhombic sulphur. The *trans* and *trans-trans* configurations correspond to parts of a helical chain.

As the studies of Foss *et al.* have been made in the solid state and partly on salts, lattice-energy relations and the coordinating power of the positive ion may be deciding factors in the choice between a *cis* or a *trans* configuration. Thus in pentathionate, selenopentathionate, and telluropentathionate of barium a *cis* form of the chain is found (129 to 135). On the other hand, ammonium telluropentathionate shows a *trans* configuration (136). A *trans* configuration has earlier been found in a molecule like sulphur dimethanethiosulphonate, $S(S_2O_2CH_3)_2$ (137). In a note on a structure analysis of the potassium barium salt of hexathionic acid ($K_2Ba\ (S_6O_6)_2$) Foss, Hordvik & Palmork (138) report to have found the *cis-cis* configuration. Previously a *trans-trans* six-membered chain has been found in cesium hexasulphide by Abrahams & Grison (139). A *trans-trans* six-membered chain also occurs in the compound *trans*-$(Coen_2Cl_2)S_6O_6 \cdot H_2O$(140).

In the course of the studies on polythionic compounds, Foss has done preliminary work on sulphur dithiocyanate, $S(SCN)_2$ (141). For an explicit study of the thiocyanate group in a covalent compound, Bringeland & Foss have carried out an x-ray structure analysis of ethylene thiocyanate (142). This molecule has a centrosymmetric *trans* form with the cyanide groups rotated out of the S—C—C—S plane. A value of 172° found for the S—C—N angle is assumed not to be significantly different from 180°.

Among inorganic molecules containing sulphur, the three-dimensional x-ray study of $S_4N_4H_4$ carried out by Sass & Donohue should be mentioned (143). Their result is very nearly the same as that of an independent two-dimensional analysis (144). The correctness of the generally assumed structure in which there is a puckered eight-membered ring of alternating sulphur and nitrogen atoms is thus well established. Packing considerations made by Sass and Donohue, indicate N—H bonds, rather than S—H bonds, in agreement with the spectroscopic studies of Lippincott & Tobin (145). The

sulphur bond angle and the dihedral angle have values close to those of $S_8$. An interesting detail of the $S_4N_4H_4$ molecule is the average value of 122.2° for the S—N—S angle which suggests the presence of trigonal planar S—NH—S groupings. The average S—N bond length of 1.674 A is about three per cent shorter than the value predicted for a single bond.

In connection with a review of sulphur-nitrogen compounds, it may be of interest to draw attention to the structure determination of platinum tetrathionitrosyl, $Pt(SN)_4$, carried out by Lindqvist & Weiss (146).[2] The $Pt(SN)_4$ molecule is found to be planar, with two SNSN chains in *cis*-position acting as bidentate ligands to the platinum atom. The average N—S bond distance is 1.58 A which is smaller than the value of 1.62 A observed by Lu & Donohue in $S_4N_4$ (147).

To judge from the number of published papers, the greater part of the activity in x-ray crystallographic structure determination is concerned with organic molecules containing a number of atoms to be localized in the range from 10 to 30. An adequate review of this field would go far beyond the limits of this article. The authors have not even tried to do justice to the highly impressive achievements reported over the last year. As mentioned in the introduction, it is fortunate however, that most results of structure determination of this kind of molecules are being published in journals easily available in laboratories where structure work is done. When details are desired, one must refer to these journals, especially *Acta Crystallographica;* only a summarized treatment of a few general trends can be given here.

Several of the structure determinations of the larger organic molecules are carried out by three-dimensional Fourier analyses which are based upon a great number of reflections, often in the range from 1000 to 2000. In one case, as many as 5527 reflections have been measured (148). This paper, which is the structure determination of p,p′-dimethoxybenzophenone by Karle *et al.*, reports also the most complex structure studied so far by the direct probability method of Hauptman & Karle. A general feature of recent work is also the extensive use of least-squares methods for the determination of the best set of parameters.

Much attention has been given to molecules of biochemical and biological importance. In this connection it seems proper to mention first the refinement of the structure of the simplest of all amino acids, glycine, reported by Marsh (149). The atoms, including hydrogen, were located from three-dimensional electron-density maps based upon 1867 observed reflections, and the standard deviations in positional parameters of the heavy atoms are found as low as about 0.001 A. The C—H and N—H distances are reported to be 0.16 A shorter than the normal single bond distance, which is believed to indicate a displacement of the effective centers of electron density of hydrogen toward the adjacent atoms.

Important contributions to the information on components of polypeptide chains are also the high quality three-dimensional structure analyses

[2] This molecule is later reported to contain two hydrogen atoms (158, 159, 160).

of two tripeptides, viz., leucyl-propyl-glycine carried out by Leung & Marsh (150), and glutathione (glutamyl-cysteinyl-glycine) by Wright (151). An interesting supplement to the latter is a paper (152) which gives a comparison of the methods used: the heavy-atom technique, the Buesger superposition method, the permutation-synthesis method, and the sign-determining methods of Cochran and Douglas and of Hauptman and Karle.

An important contribution to our knowledge of protein molecules was made last year when Kendrew *et al.* were able to build a three-dimensional model of the myoglobin molecule, based upon a three-dimensional x-ray analysis with a resolution of 6 A (153).

A review article (154) which summarizes the situation of molecular biology was written by Perutz, who himself has decisively advanced the work in this field with the introduction of the method of isomorphous replacements of heavy atoms (155). Also Bodo gives a comprehensive report on the x-ray structure analysis of proteins (156). The authors also wish to draw attention to a review on the masterpiece of modern x-ray crystallography, the structure determination of vitamin $B_{12}$, by Hodgkin (157).

With respect to structure determinations of more average-sized organic molecules, the authors feel that the best they can do is to refer to *Acta Crystallographica* and other well-distributed journals. Much interesting work has been done on different classes of compounds: on alkaloids and other heterocyclic compounds, on long-chain carboxylic acids, and on condensed aromatic systems. In this work lies a great quantity of structural information. Generally, however, the results found are not unexpected from a chemical point of view.

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# THE KINETICS OF REACTIONS IN GASES[1]

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During 1958 a book on the kinetics of homogeneous gas reactions was published by Kondratiev (1). In addition, two independent translations of the first part of Semenov's book (2, 3) of 1954, slightly modernised by the author, and two symposia on gas kinetics (4, 5) appeared. Semenov's book was originally written, with the help of several colleagues, as an introduction to a symposium. Therefore, it properly attempts to raise points for discussion rather than to present a full critical survey of gas kinetics. The papers in the symposium were chiefly short reviews of the authors' work which have been or will be published elsewhere. Kondratiev's book, on the other hand, is a comprehensive survey of the whole field. It is interesting to note that approximately one-quarter of the references in it are taken from the Russian literature. In this respect, the shortcomings of this review will be obvious. The language difficulty is aggravated by the inaccessibility of some of the Russian journals and by the fact that comparatively few of them become available during the year in which they are published.

No revolutionary developments in gas kinetics have occurred during the year, although much solid progress has been made, particularly in the study of elementary reactions. For the first time, however, large numbers of papers have been published that report work in which gas chromatography has been used for analyses. The development of gas kinetics has always been closely linked to the progress of analytical techniques. The application of gas chromatography has made possible the investigation of many new systems (particularly those involving less volatile materials) and the far more detailed study of familiar reactions.

Before considering the year's work in detail, one general remark may be made. It would be of great assistance to reviewers and others if authors who report results in terms of the Arrhenius or similar equations would always give values of both the activation energies and the $A$ factors (or the $A$ factor ratios). It is tedious to have to work back from selected rate constants and, worse still, from steric factors (the collision diameters assumed are frequently not reported).

## Theory

The most progress has been made in the understanding of the processes of the transfer of energy from molecules containing sufficient energy to react. Bunker & Davidson (6) assumed that MI complexes were first formed in the combination of iodine atoms in the presence of a third body, M. Good agreement with experiment was obtained if there was a Lennard-Jones potential

[1] The survey of literature was completed on November 15, 1958.

between M and I for chemically inert substances. The relationship broke down as might have been expected for hydrogen, deuterium, and helium. It was assumed that iodine molecules formed a chemical bond with the atoms, with a strength of about 5 kcal. $mole^{-1}$.

Mahan (7) successfully applied a theory (8), originally developed to deal with molecules containing a few vibrational quanta, to the transfer of energy from activated nitryl chloride.

A few attempts (9, 10, 11) have been made to calculate the rates of simple chemical reactions and, in particular, transfer reactions (that of hydrogen atoms with hydrogen) with the aid of very fast digital computers. Their great speed makes it possible to explore a greater number of variables and to apply a statistical treatment. Reasonable results have been obtained, but the difficulties presented by the more complex systems that are of wider interest are enormous. There was fair agreement with the calculations made before the advent of the fast computers.

There appears to be some hope of a substantial advance in our understanding of the $A$ factors of metathetical reactions owing to the much more accurate experiments that are being done. Soon it should be possible to assess theoretical predictions of $A$ factors and, particularly, $A$ factor ratios with some confidence.

Szwarc & Herk (12) suggested how the exothermicity of the third stage of the sequence:

$$ABC \rightarrow AB + C \rightarrow A + B + C$$

might lower the activation energy of the first step below the bond strength. A related problem is that of the reactions with activation energies that are considerably greater than the strength of the weakest bond in the molecule. Such reactions are usually found to have exceptionally high $A$ factors.

## Energy Transfer

Several important papers on ultrasonic dispersion, of great interest to the kineticist, have been published but are not reviewed now because they do not come strictly under the heading of reactions.

The use of flash photolysis in the study of energetic problems has been reviewed by McGrath & Norrish (13, 14). The important problem of the rates of combination of atoms in the gas phase appears to be nearer solution, now that accurate data are becoming available for several types of atoms and the variation of rates with temperature is being studied. Iodine atoms have been most frequently investigated; but Bunker & Davidson (15), using a flash technique, have provided the first accurate study of temperature coefficients for several reactions of the type:

$$I + I + M = I_2 + M$$

Their results fit the following Arrhenius parameters:

| M | Ar | $C_4H_{10}$ | $I_2$ |
|---|---|---|---|
| log $A$/mole$^{-2}$l.$^2$ sec.$^{-1}$* | 8.67 | 9.36 | 8.3 |
| $E$/kcal. mole$^{-1}$ | −1.13 | −1.65 | −5.2 |

* Throughout this article nomenclature such as this is used. The meaning is as follows: log A/mole$^{-2}$ l.$^2$ sec.$^{-1}$ means logarithm of the quantity A whose units are mole $^{-2}$ l.$^2$ sec.$^{-1}$; also, E/kcal. mole$^{-1}$ means the quantity E has units of kcal mole$^{-1}$.

Reasonably concordant rate constants of about $10^{16}$ mole$^{-2}$ cm.$^6$ sec.$^{-1}$ for the combination of nitrogen atoms in the presence of nitrogen have been obtained by three independent groups of workers, using two different methods (16, 17, 18). Argon is 0.61, and helium 0.15, times as efficient a third body as nitrogen. Golden & Myerson (19) found that, in the presence of 4 mm. of oxygen, oxygen atoms followed by flash spectroscopy combined with a rate constant of $10^{14.5}$ mole$^{-2}$ cm.$^6$ sec.$^{-1}$.

All atomic combinations are highly exothermic and many yield excited molecules that will emit detectable radiation. One instance of this is the strong infra-red emission attributable to excited HCl molecules, which is observed when hydrogen atoms combine in the presence of chlorine (20). Sodium resonance radiation is emitted when sodium atoms are fed into a steam of atomic hydrogen. The two possible sources of the excited atoms are:

$$2\,Na + H = NaH + Na^*$$

which would have a collision yield of $10^{-2.4}$ (21) or

$$Na + 2H = H_2 + Na^*$$

which would have a collision yield of $10^{-5}$. McGrath & Norrish (22) found that vibrationally excited oxygen molecules in the ground state, formed by the reaction of oxygen atoms with ozone, would induce the decomposition of ozone.

Kaufman (23) produced oxygen atoms by the microwave dissociation of the molecules in a flow system. The atomic concentration could be measured by the glow emitted when they reacted with nitric oxide and absolutely determined by titration with nitrogen dioxide. The third body reactions, with nitric oxide to give nitrogen dioxide and with oxygen to give ozone, have rate constants of $10^{16.4}$ and $10^{14.6}$ mole$^{-2}$ cm.$^6$ sec.$^{-1}$, respectively. The latter rate constant is increased by a factor of ten in the presence of carbon dioxide.

Schott & Davidson (24) studied the classic unimolecular decomposition of nitrogen pentoxide by a shock wave technique between 450° and 550°K. in the presence of about 0.0076 mole l.$^{-1}$ of argon. They confirmed Johnston's (25) estimates of the rate constants of the principal elementary reactions by direct measurement and were able to clear up most of the remaining uncertainties about the reaction. In particular, they deduced that nitrogen

trioxide has a heat of formation of 17.1 kcal. $mole^{-1}$ and an entropy of 60 cal. $mole^{-1}$ $deg.^{-1}$. The history of the pentoxide decomposition exemplifies the way in which a problem is elucidated by the successive application of fresh techniques.

Another classic reaction that is still being fruitfully studied is the isomerization of cyclopropane. Rabinovitch, Schlag & Wiberg (26) measured the rates of both the geometrical and structural isomerization of *trans*-cyclopropane-$d_2$. The rates of the two reactions were very similar and appeared to vary with pressure in much the same way. This finding is most readily interpreted by supposing that trimethylene is formed as an intermediate, a mechanism that had previously been rejected on the basis of Slater's calculations (27) which only agreed with the experiment if the critical coordinate was a C—H distance. Smith (28) suggested that the two findings might be reconciled if the critical hydrogen was placed in the plane of the cyclopropane ring in the activated complex. It appears that this point could be elucidated by experiments with deuterated methylcyclopropane, but the compound would be difficult to prepare and might not react in the expected way. Evidence obtained by Langrish & Pritchard (29) on the relative rates of isomerization and decomposition of normal and deuterated cyclopropane and cyclobutane do not provide unambiguous evidence on the mechanisms.

The addition of methylenes to olefins yields activated cyclopropanes that readily isomerize. Cyclopropane and methylcyclopropane formed in this way have been studied by Frey & Kistiakowsky (30) and 1,1-dimethylcyclopropane by Knox, Trotman-Dickenson & Wells (31). Although the results are in general agreement with expectations, a full theoretical treatment encounters many uncertainties as to the steps by which the molecules are deactivated.

The reactions of three other types of molecules synthesized in activated forms have been investigated. Wilson & Kistiakowsky (32) have measured the rate of association of methylene with carbon monoxide, relative to the rate of formation of ethylene with ketene, by photolysing ketene in the presence of $^{13}CO$. The activated ketene is stabilized by collision with a second ketene molecule with 1.25 times the efficiency for a collision with sulfur hexafluoride and ten times the efficiency for nitrogen. Methyl iodide is about ten times as efficient as carbon dioxide in stabilizing the methylperoxy radical derived from the reaction of methyl, from the photolysis of methyl iodide, with oxygen [Christie (33)]. The ratio $k_1/k_2$ is $10^{3.7}$ $mole^{-1}$ $cm.^3$ with methyl iodide as the third body.

$$CH_3 + O_2 + M = CH_3OO + M' \qquad 1.$$

$$CH_3 + I_2 = CH_3I + I \qquad 2.$$

Berisford & LeRoy (34) have estimated that the methane molecule, formed by the combination of methyl with a hydrogen atom, has a lifetime of $10^{-9}$ sec. In the study of the effect of pressure on the rate of pyrolysis of hydrogen peroxide, Forst (35) has found that, relative to the peroxide, water has ef-

ficiency in energy transfer of 0.75; oxygen, of 0.15; and helium, of 0.11. His results can be interpreted in terms of the Kassel theory only if the number of effective oscillators is three with helium, but five with hydrogen peroxide. A somewhat analogous behaviour has been observed in studies of the pyrolysis of bromine at very high temperatures. Blades (36) has detected a pressure dependence in the rate constant for the elimination of hydrogen bromide from ethyl bromide in the presence of toluene.

The homogeneous decomposition of chlorine heptoxide, whose high pressure rate constant is given by

$$\log k/\text{sec.}^{-1} = 15.7 - (32900/2.3RT),$$

has been interpreted in terms of a molecule with 21 degrees of freedom [Figini, Coloccia & Schumacher (37)].

Birss (38) has reported a most unusual type of pressure dependence for the rate of decomposition of di-*t*-butyl peroxide in the presence of sulfur hexafluoride and other inert gases. It would seem that satisfactory results on energy transfer can only be obtained with the simplest systems.

### Radical Decompositions and Combinations

Less work than usual has been reported on reactions involving the rupture of a single bond and has been concerned principally with the pyrolyses of the metallic alkyls. Using the toluene carrier technique, Cowperthwaite & Warhurst (39) found that

$$\log k/\text{sec.}^{-1} = 15.7 - (63200/2.3RT)$$

for the decomposition of phenyl mercuric iodide. Price & Trotman-Dickenson (40) found the following rate constants which were identified with the rate of fission of the first metal-carbon bonds:

| | | |
|---|---|---|
| For $BiMe_3$ | $\log k/\text{sec.}^{-1}$ = | $14.02 - (44030/2.3RT)$ |
| for $SbMe_3$ | " | $15.2 - (57000/2.3RT)$ |
| for $SnMe_2Cl_2$ | " | $13.52 - (56100/2.3RT)$ |

all at about 16 mm. Srinivasan (41) drew attention to the importance of heterogeneous reactions when dimethyl mercury is pyrolysed in a static system. Laurie & Long (42) found that the pyrolysis of dimethyl cadmium in a static system was also heterogeneous; but by using reaction vessels of different dimensions, they were able to obtain a value of the homogeneous rate constant at one temperature which was in reasonable agreement with that which could be deduced from Price & Trotman-Dickensons (43) work in a flow system.

Wegener (44) studied the rate of decomposition of nitrogen tetroxide in a stream of nitrogen at a supersonic nozzle between 220° and 300°K. His results were rather scattered but agreed generally with those of other workers.

Much more work has been done on radical combinations. Moseley & Robb (45) followed the nonstationary state kinetics of the photolysis of acetone with a diaphragm manometer. They found a rate constant for the

combination of methyls in reasonable agreement with previous workers. Unfortunately, their method would not seem to be readily adapted to the measurement of activation energies. Using the conventional rotating sector technique, McDowell & Sharples (46) found that at 20°C. the rate constants for the mutual destruction of acetylperoxy and propionylperoxy radicals were $10^{14}$ and $10^{13.4}$ mole$^{-1}$ cm.$^3$ sec.$^{-1}$, respectively. Although the dimers are not isolable, the first step may have been a combination reaction.

Kraus & Calvert (47) have suggested that the simple numerical relations between the relative rate constants for the combination and disproportionation of the propyl and butyl radicals are evidence that all the rate constants are the same. Some suport for this view may be seen in the information on the rates of cross-combination of radicals A and B ($k_{ab}$) as compared with the

TABLE I

CROSS-COMBINATION OF RADICALS

| Radicals | $k_{ab}/(k_{aa}k_{bb})^{1/2}$ | Source |
|---|---|---|
| Methyl+Ethyl | 2.0 | Heller (48) |
| Methyl+*n*-Propyl | 2.5 | McNesby & Gordon (49) |
| Methyl+Methoxyl | 1.9 | Wijnen (50) |
| Methyl+Acetyl | 1.7 | Wijnen (50) |
| Ethyl+*n*-Propyl | 1.9 | Kerr & Trotman-Dickenson (51) |
| Ethyl+*s*-Propyl | 2.05 | Kerr & Trotman-Dickenson (51) |
| | 2 | Wijnen (52) |

rates of auto-combination $k_{aa}$ and $k_{bb}$, which has recently become available (see Table I). All these values closely approach the relative collision frequencies.

Thrush (53) has suggested that methyl radicals may be produced in the interaction of two ethyl radicals if one of them is excited. The rates of combination of oxygen atoms with both nitric oxide and nitrogen dioxide, which require the presence of a third body, have been measured (54, 55).

## MOLECULAR DECOMPOSITIONS

A number of reactions have been studied in which a molecule decomposes without the intervention of free radicals. Some of the Arrhenius parameters that have been obtained are listed in Table II.

Maccoll & Stimson (65) reported that the molecular elimination of water from *t*-butyl alcohol is catalysed by hydrogen halides. The catalysed reaction is homogeneous and first order with respect to the alcohol and the halide. This is the first occasion on which acid catalysis in the gas phase has been observed. The relative efficiencies of HCl, HBr, and HI are 0.04:1:8 at 320° C. There is a good linear relation between the logarithm of the efficiency and the energy of ionization of the halide.

TABLE II

RATE FACTORS FOR MOLECULAR DECOMPOSITIONS

| Reactant | log $A$ sec.$^{-1}$ | $E$ kcal. | Source |
|---|---|---|---|
| Methylcyclobutane | 15.4 | 61.2 | Das & Walters (56) |
| Methylcyclobutylketone | 14.5 | 54.5 | Daignault & Walters (57) |
| Ethyl bromide | 12.9 | 52.2 | Blades (58) |
| Ethyl bromide-$d_5$ | 13.3 | 54.8 | Blades (58) |
| *n*-Propyl bromide | 12.9 | 50.7 | Maccoll & Thomas (59) |
| *n*-Butyl bromide | 13.2 | 50.9 | Maccoll & Thomas (59) |
| *s*-Butyl bromide | 13.5 | 46.5 | Kale, Maccoll, & Thomas (60) |
| *t*-Amyl bromide | 13.6 | 40.5 | Harden (61) |
| Cyclopentyl bromide | 12.8 | 43.7 | Kale & Maccoll (62) |
| 2-Bromo-2,3-dimethyl butane | 13.5 | 39.0 | Harden & Maccoll (63) |
| Cyclohexyl chloride | 13.8 | 50.0 | Swinbourne (64) |

Maccoll (66) has discussed the elimination of olefins from esters and concluded that they are probably six-centre reactions, whereas the decompositions of the alkyl halides are four-centre reactions.

The rate constant for the isomerization of cyclobutene to butadiene is given by (67)

$$\log k/\text{sec.}^{-1} = 13.1 - (32500/2.3RT).$$

The *cis-trans*-isomerization of 2-butene has been reinvestigated and found unexceptional. The rate constant is given by (68)

$$\log k/\text{sec.}^{-1} = 11 - (52000/2.3RT).$$

It now seems very unlikely that any of the *cis-trans*-isomerizations have very low $A$ factors; with the aid of modern analytical methods, several of the original investigations have been shown to be in error.

## CHAIN DECOMPOSITIONS

The nonstationary state kinetics of chain reactions have been discussed by Goodall (69), but comparatively few systems to which the treatment could properly be applied have yet been studied. Wilson (70) has considered the temperature gradients that may be set up in reaction cells by exothermic processes.

The relative efficiencies of olefins as chain inhibitors in the decomposition of *n*-propyl bromide have been measured by Maccoll & Thomas (59), who found that their activities were in the ascending order: Propylene, 500: Dimethyl-pent-2-ene, 400:Cyclohexene, 100:Cyclopentadiene, 40. The figures represent the pressure of the olefin required to produce a standard degree of inhibition.

Freeman, Danby & Hinshelwood (71) have studied the complex decom-

positions of diethyl ether and acetaldehyde. The rate constants in the presence and absence of nitric oxide were obtained from pressure measurements, although extensive analyses were also performed. The reactions cannot yet be satisfactorily interpreted in terms of the elementary steps. The thermal decomposition of pentachlorethane is more straightforward, and a reasonable mechanism has been proposed by Houser & Bernstein (72). Cullis & Manton (73) have demonstrated the complexity of the pyrolysis of chlorobenzene, even when followed in a flow system. Among the other compounds that have been conventionally pyrolysed, but for which no complete mechanism can be written, are: ketene (74), methyl *n*-propyl ketone (75), ethylene (76), and decaborane (77).

Shock wave techniques have been used to study the decompositions of hydrocarbons (78) and water (79) at temperatures between 1600° and 3200°K. Unfortunately, the interpretation of the results is not straightforward.

## Transfer Reactions

The year's work on atomic reactions has been characterized by solid progress in the study of halogen atoms made possible by improved analytical techniques and by a considerable advance in the understanding of the reactions of nitrogen and oxygen atoms.

Benson & Buss (80) have pointed out the importance of nonsteady state kinetics and heterogeneous reactions in halogenations. It seems that these matters have previously been accorded insufficient attention. The kinetics, thermodynamics, and transport properties of the hydrogen-bromine system have been extensively reviewed by Campbell & Fristrom (81). Levy (82) has shown that the accepted mechanism for the hydrogen-bromine reaction at low temperatures holds up to 1200°K. in a flow system. Goldfinger *et al.* (83, 84) have discussed their own extensive work on chlorinations in terms of transition state theory and correlated the results with those of other workers. Some of the results have not previously been published and are noted below:

| Reaction | log $A$/mole$^{-1}$ l. sec.$^{-1}$) | $E$ (kcal.) |
|---|---|---|
| $CH_2Cl_2+Cl=CHCl_2+HCl$ | 11.6 | 5.5 |
| $CHCl_3+Cl=CCl_3+HCl$ | 11.6 | 6.5 (85) |
| $C_2HCl_5+Cl=C_2Cl_5+HCl$ | 10.9 | 5.4 |

Engelsma & Kooyman (86) found that the bromination and chlorination of halobenzenes and benzonitriles yields surprisingly large amounts of *meta*-substituted products. This is some of the first work on the metathetical reactions of the benzene nucleus in the gas phase, and it is to be hoped that the field will soon be fully explored. Tedder & Anson (87) measured the relative rates of attack of chlorine and fluorine on the different positions in *n*-butane and isobutane. As would be expected, the fluorine atoms are very unselective in their attack.

Norrish & Purnell studied the mercury photosensitized decomposition of *n*-hexane (88) and the reactions of *n*-hexane with hydrogen atoms produced by the mercury photosensitized decomposition of hydrogen (89). They estimated the rate of attack of hydrogen atoms, assuming that the presence of the hexane did not affect their concentration. This would only be true if the reaction of hexyl with molecular hydrogen is very fast, a possibility which they rightly reject. Thus, little value can be attached to their main conclusion. It has been shown that hydrogen atoms form hydrogen cyanide with amines (90).

The rates of reaction of nitrogen atoms with cyclopropane, cyclobutane, and cyclopentane have been reported to increase in this order (91). The results indicate that this gradation is to be attributed entirely to the $A$ factors; the trend of the activation energies is in the opposite direction. The reactions of nitrogen atoms with chloromethanes have been studied by similar methods (92).

Limits have been placed by Kistiakowsky & Volpi (93) on the rates of reaction of nitrogen atoms with nitrous oxide, nitric oxide, and nitrogen dioxide. Hydrogen, carbon monoxide, and ammonia were found to be unreactive (94). Harteck & Dondes (95) found that the reaction of nitrogen atoms with nitrogen dioxide formed nitrous oxide, nitric oxide, and nitrogen in the proportions of 2:3:10.

Less work on oxygen atoms has been reported. Ford & Endow (96) found the following rate constants at room temperature:

| | |
|---|---|
| $O + NO_2 + M = NO_3 + M$ | $k = 10^{11.0}$ mole$^{-2}$ l.$^2$ sec.$^{-1}$ |
| $O + NO_2 = NO + O_2$ | $k = 10^{9.3}$ mole$^{-1}$ l. sec.$^{-1}$ |
| $O + NO + M = NO_2 + M$ | $k = 10^{10.3}$ mole$^{-2}$ l.$^2$ sec.$^{-1}$ |

They also established rate constants for the less well characterized reactions with *n*-butane, acetaldehyde, ethylene, and isobutene (97). The olefins, however, probably react by abstraction to only a small extent. Kaufman (23) found rate constants for the reaction of oxygen atoms with hydrogen ($10^{7.5}$ mole$^{-1}$ cm.$^3$ sec.$^{-1}$) and chlorine ($10^{10.8}$) at room temperature. Both nitrogen and oxygen atoms are involved in the reaction of oxygen with nitrogen at 2000°–3000°K. in a shock tube, but little can be said about the elementary rate constants (98). McGrath & Norrish (99) have suggested that O($^1$D) atoms are produced by the flash photolysis of ozone and that the reaction of these atoms with water yields hydroxyl radicals. They ascribe the aqueous catalysis of the photolytic decomposition of ozone to this reaction.

An increasing amount of work is being done on the reactions that involve the oxides of chlorine. OCl radicals are involved in the flash photolysis of chlorine monoxide, as they are in the photolysis of mixtures of chlorine and oxygen, and chlorine dioxide (100). At room temperature, the rate constants of the transfer reactions are as follows:

| | |
|---|---|
| $Cl + Cl_2O = Cl_2 + ClO$ | $k > 10^{8.6}$ mole$^{-1}$ l. sec.$^{-1}$ |
| $2\ ClO = Cl_2 + O_2$ | $k = 10^{7.4}$ |
| $OCl + Cl_2O = ClO_2 + Cl_2$ | $k = 10^{5}$ |
| $OCl + Cl_2O = Cl + O_2 + Cl_2$ | $k = 10^{4.7}$ |

OCl is also involved in the reactions of nitrogen dioxide with chlorine dioxide, chlorine monoxide, and nitrosyl chloride (101, 102). The following rate constants have been determined:

$$NO_2 + NOCl = NO + NO_2Cl \qquad \log k = 7.3 - (10000/2.3RT)$$
$$NO_2 + ClO_2 = NO_3 + OCl \qquad \log k = 7.4 - (11000/2.3RT)$$
$$NO_2 + Cl_2O = NO_2Cl + OCl \qquad \log k = 6.8 - (10500/2.3RT)$$

The OCl radical has also been discussed as an intermediate in the halogen catalysed decomposition of nitrous oxide (103).

Rice & Vanderslice (104) have obtained some of the first really satisfactory figures on the relative rates of attack of methyl radicals on primary, secondary, and tertiary hydrogens in hydrocarbons by reacting radicals from the decomposition of azomethane with partially deuterated hydrocarbons. They found that the activation energy for the attack on a primary atom is 2.3 kcal. mole$^{-1}$ greater than that for attack on a secondary, which is 0.6 kcal. mole$^{-1}$ higher than for attack on a tertiary atom. They also found that attack on deuterium atoms requires 0.7 kcal. mole$^{-1}$ more energy than attack on equivalent hydrogens. Wijnen (105, 106) found that the attack by methyl on methyl-$d_3$ acetate to yield $CH_4$ has an activation energy of 10.0 kcal. mole$^{-1}$, whereas the formation of $CH_3D$ required 14 kcal. mole$^{-1}$. The reaction with ethyl propionate has an activation energy of 8.2 kcal. mole$^{-1}$ (107). The abstraction of hydrogen by methyl from crotonaldehyde proceeds at nearly the same rate as abstraction from acetaldehyde (108). The suggestion of Long (109), that the reaction of methyl with ethane plays a significant role in the normal photolytic systems in which methyl reactions (particularly with hydrogen) are usually studied, has been effectively dismissed by Kutschke & Steacie (110).

The Arrhenius parameters of a considerable number of the abstraction reactions of ethyl radicals have been measured (see Table III).

TABLE III

RATE FACTORS FOR ABSTRACTION OF HYDROGEN BY ETHYL RADICALS

| Reactant | Ref. | log $A$/mole$^{-1}$ cm.$^3$ sec.$^{-1}$ | $E$/kcal. mole$^{-1}$ |
|---|---|---|---|
| Diethyl ketone | (111) | 12.0 | 8.8 |
| 1-heptene | (111) | 11.8 | 9.3 |
| 1-octene | (111) | 11.8 | 9.3 |
| Cyclohexene | (111) | 12.1 | 9.2 |
| 4-octene | (111) | 12.0 | 9.7 |
| *n*-heptane | (111) | 12.3 | 11.6 |
| 1-heptyne | (111) | 12.5 | 8.6 |
| Diethyl ketone-$d_{10}$ | (112) | 12.2 | 10.6 |
| Ethyl propionate | (113) | 12.1 | 10.8 |
| Azoethane | (114) | 11.9 | 9.0 |

Heller & Gordon (115) have found that *s*-propyl radicals abstract hydrogen atoms from di-isopropyl ketone at the following rates, assuming that the rate of combination is $10^{14}$ mole$^{-1}$ cm.$^3$ sec.$^{-1}$:

$$\alpha\text{-hydrogen} \quad \log k = 11.1 - (9300/2.3RT)$$
$$\beta\text{-hydrogen} \quad \log k = 11.8 - (11700/2.3RT).$$

Perfluoro-di-*n*-propyl ketone has been shown (116) to be an excellent source of $C_3F_7$ for the study of abstraction reactions. Acetyl peroxy and propionyl peroxy radicals react with their photo-oxidized parent aldehydes with activation energies of 7.2 and 6.8 kcal. mole,$^{-1}$ respectively (46).

The results that have been obtained on disproportionations, which can be conveniently expressed in terms of their rate constants relative to those for combination, are listed in Table IV.

TABLE IV

RELATIVE RATES OF DISPROPORTIONATION AND COMBINATION OF RADICALS

| Radicals | $k_{disp.}/k_{comb.}$ | Source |
|---|---|---|
| Methyl+Ethyl | 0.06 | Heller (48) |
| Methyl+Methoxyl | 1.4 | Wijnen (117, 118) |
| Methyl-$d_3$+Methoxyl-$d_3$ | 1.8 | Wijnen (118) |
| Ethyl | 0.14 | James & Stacie (111) |
| | 0.12 | Cerfontain & Kutschke (114) |
| Ethyl-$d_5$ | 0.14 | James & Steacie (112) |
| *s*-Propyl | 0.63 | Heller & Gordon (115) |
| Isobutyl | 0.41 | Kraus & Calvert (47) |
| *s*-Butyl | 2.27 | Kraus & Calvert (47) |
| *t*-Butyl | 4.59 | Kraus & Calvert (47) |
| Mixed pentyl | 2.0 | Back (119) |

Pitts and his co-workers (120, 121) have established that a displacement reaction occurs, yielding butene, when methyl reacts with methyl propenyl ketone or crotonaldehyde. It appears doubtful whether the thermal exchange between methyl iodide and radioactive iodine is a displacement reaction or a four-centre exchange with a rate constant given by (122)

$$\log k/\text{mole}^{-1}\ \text{cm}^3\ \text{sec.}^{-1} = 6.4 - (9000/2.3RT).$$

It has been suggested by Neill & Kahn (123) that the very low $A$ factor of 0.17 mole$^{-1}$ l. sec.$^{-1}$, that they found for the four-centre exchange between hydrogen chloride and acetyl chloride, can be attributed to a pre-equilibrium. Howard & Daniels (124) have found no nitrogen dioxide in specimens of nitric oxide that were sealed up 40 years ago. This is not surprising, because an extrapolation from high temperature work indicates that $10^{29}$ years would have to elapse before considerable decomposition could be expected.

It is now clear that the reaction of hydrogen with nitrogen dioxide, which was once thought to be a simple transfer reaction, is a chain reaction. Ashmore & Levitt (125) have determined the ignition limits for mixtures between 516° and 570°C. and found that they can be related to the kinetics at about 400°C.

## Excited Species in Gas Kinetics

Increasing attention has been paid in recent years to the role played by excited species in the mechanism of gas reactions. This development can be partially ascribed to the general improvement in techniques of investigation that makes it possible to detect with certainty the effects which frequently are small. The use of flash photolysis and other light sources of high intensity, coupled with spectrographs of great resolving power, have made the direct detection of excited species a simpler matter. During the year, several papers on such species and also on photosensitization have been published. Some will be considered here; others have already been mentioned.

Gunning (126) has given a general review of work that he and his collaborators have recently done on mercury photosensitization using resonance lamps made with isotopically enriched mercury. He has studied the enrichment that can be obtained with $^{202}Hg$ in systems in which mercury is mixed with different gases that yield involatile mercury-containing products. The greatest enrichment was found with water-butadiene mixtures. The enrichment with alkyl halides and hydrogen chloride is markedly less.

The reinvestigation of several of the simpler, mercury photosensitized systems (such as the higher paraffins), with the aid of gas chromatography, should be well worth while. Back (119) has studied the mercury photosensitized decomposition of *n*-pentane, but without full analyses at 20°C. He found that hydrogen was produced but detected no hydrocarbons containing less than five carbon atoms. Better analytical techniques should enable workers to be sure whether excited mercury atoms can cause a paraffin chain to rupture and to ascertain the position from which hydrogen atoms are most readily removed. Luner & Gesser (127) found that the chief products of the mercury photosensitized decomposition of ethylene imine between 25° and 175°C. to be ethylene and hydrogen in equal quantities, together with a smaller amount of nitrogen. No full and satisfactory reaction scheme could be devised. The photosensitized polymerization of acetylene (128) yields benzene, hydrogen, and polymer. About one-third of the acetylene consumed forms benzene. The over-all quantum yield is 4.8. None of these systems is fully understood; still more detailed analyses of the products is required.

The quenching of the iodine fluorescence spectrum excited by radiation from a mercury arc has been reinvestigated along lines similar to those originally employed by Rössler and Eliasevitch. Values were obtained for the rate constants for the transfer of vibrational energy from the electronically excited iodine molecules to helium, neon, argon, and oxygen, relative

to the rate constant for the fluorescent decay. The transfer of energy is very efficient, in contrast to the transfer of energy from the lower vibrational levels in the ground state (129, 130, 131).

Much interesting work remains to be done on the properties of the excited species initially formed when light is absorbed by such common photolytic sources as aldehydes and ketones. Unsaturated ketones seem to be peculiarly resistant to radical fission. Tolberg & Pitts (132) found that, up to 275°C., the irradiation of methyl-*trans*-propenyl ketone with light of 3130 A produced virtually no radicals, but only *cis-trans* isomerization. With light of 2380 A, the quantum yield of carbon monoxide was greater than unity. Hexafluoroacetone yields excited molecules that have sufficiently long lifetimes that they can be deactivated, and they may fluoresce rather than decompose (133). The importance of activated molecules, with comparatively long lifetimes, in the photolysis of acetone has been known for many years. It is particularly apparent in the photolysis using a high-intensity spark source giving light of about 2800 A (134). Some of the molecules decompose spontaneously into methyl and acetyl, whereas others yield two methyl radicals and carbon monoxide on collision with a normal acetone molecule.

The primary process in the photolysis of (+) *s*-valeraldehyde has been investigated by Gruver & Calvert (135) who added iodine to the system in the hope that it would combine with any radicals that were formed. The analyses of the products indicated that between 48° and 128°C. the quantum yields at 3130 A were as follows:

| Products | Quantum Yield |
|---|---|
| Butyl+formyl | 0.60 |
| Ethylene+propionaldehyde | 0.17 |
| Butane+carbon monoxide | 0.003 |

McNesby & Gordon (136) photolysed 2-pentanone-1,1,3,3,3-$d_5$ and found that acetone and ethylene were primary products whose proportions varied with the intensity of the illumination. The ethylene contained little deuterium. Considerable quantities of acetone-$d_6$ that could not be formed by an intramolecular reaction were found. The photolysis of 2-hexanone similarly yields equal quantities of acetone and propylene with a quantum yield of about 0.48, as well as free radicals [Brunet & Noyes (137)]. Ausloos (137) reported preliminary results on the photolyses of several alkyl esters, XCOOY. They decomposed by molecular rearrangement to yield (*a*) XCOOH and alkene, (*b*) $CH_3COOY$ and alkene, and (*c*), to a small extent, HCOOY and alkene. They also decomposed into radical fragments as (*a*) XCO and OY, (*b*) X and COOY, and (*c*) XCOO and Y. These findings are in general agree-

ment with those of Wijnen that have already been mentioned in this review in other connections. Dorfman (139) used ethylene and propylene as free radical scavengers to show that 66 per cent of the hydrogen that is formed by the radiolytic decomposition of ethane into ethylene and hydrogen at room temperature comes from a molecular elimination. Considerable quantities of methane were also formed that were not products of a methyl radical reaction. It was suggested that they came from:

$$C_2H_5 + C_2H_6 = C_3H_5 + CH_4$$

From time to time, reports have appeared that the reactivity of radicals in metatheses depends upon the energy dissipated in their formation. McElcheran, Wijnen & Steacie (140) found that the rate of reaction of methyl radicals from the photolysis of methyl cyanide with light of 1849 A depended on the pressure in the system. This finding could be interpreted in terms of excited methyl radicals.

## The Decomposition of Radicals and the Addition of Radicals to Unsaturated Compounds

The problem of the decomposition of radicals and of their addition to unsaturated compounds remains one of the most difficult in the study of elementary reactions. The difficulty stems from the need to measure the concentration of the primary radical and the rate of formation of the radical product. Both of these quantities must be measured indirectly. The problem is somewhat less acute when chain systems are involved, as is shown by the substantial body of information about polymerizations that has been collected.

Goldfinger and his collaborators (84) have briefly reported results of experiments on the rate of the addition of chlorine to chloroethylenes. They find that for:

$$Cl + C_2Cl_4 = C_2Cl_5,$$
$$\log k/\text{mole}^{-1}\,\text{l. sec.}^{-1} = 8.4 + (500/2.3RT)$$

The chain addition of chlorine to trifluorochloroethylene (141) has also been studied, but the rates of the elementary reactions have not been determined. The over-all rate is independent of the olefin pressure between 25 and 400 mm., and varies with the three-halves power of the chlorine pressure and the one-half power of the intensity of the absorbed light. The chain length was about $10^{5.7}$ units.

In order to get over the difficulty of measuring the number of radicals formed by the addition of ethyls to olefins, James & Steacie (111) used a method based on striking a material balance for the ethyl radicals released into the system. Those that could not be otherwise accounted for were assumed to have added to an olefin. They found the Arrhenius parameters listed in Table V. A good straight line relation was found to exist between the activation energies of six of the addition reactions and the ionization po-

TABLE V

RATE FACTORS FOR THE ADDITION OF ETHYL RADICALS TO OLEFINS

| Reactant | log $A$/mole$^{-1}$ cm.$^3$ sec.$^{-1}$ | $E$/kcal. mole$^{-1}$ |
|---|---|---|
| 1-heptyne | 12.2 | 9.8 |
| 1-heptene | 11.3 | 8.0 |
| 1-octene | 11.1 | 7.7 |
| 1-hexene | 11.2 | 7.8 |
| 2,4,4-trimethyl-1-pentene | 10.8 | 6.7 |
| 2,3,3-trimethyl-1-butene | 10.4 | 6.6 |

tentials of structurally analogous compounds. Cerfontain & Kutschke (114) found that the rate constant for the addition of ethyl to azoethane is given by

$$\log k/\text{mole}^{-1}\ \text{cm.}^3\ \text{sec.}^{-1} = 10.4 - (7000/2.3RT)$$

The rate constants of the elementary processes cannot be derived from Silcocks' (142) study of the thermal polymerization of acetylene between 352° and 472°C. The reaction was completely inhibited by 0.3 per cent of nitric oxide.

Information on the decomposition of radicals is gradually being accumulated by the application of improved methods of analysis. Since only comparatively large radicals decompose at low temperatures, sources of such radicals must be found. They are not readily available because, as mentioned in the previous section, the photolyses of compounds that might be expected to yield large radicals generally yield many other products as well. These products are similar to those formed by the radical decompositions; hence, the interpretation of the analyses is difficult.

Di-isopropyl ketone is a comparatively clean source of *s*-propyl radicals. Heller & Gordon (115) have used it to measure the rate constant of the radical decompositions. If the rate constant for the combination of the radicals is $10^{14}$ mole$^{-1}$ cm.$^3$ sec.$^{-1}$, the Arrhenius parameters for the decompositions are:

| | | |
|---|---|---|
| $C_3H_7 = CH_3 + C_2H_4$ | log $A$/sec.$^{-1}$ 12.03 | $E$/kcal. mole$^{-1}$ 32.5 |
| $= H + C_3H_6$ | 13.07 | 35 |

The measurement of the rate constant of the first reaction is of particular interest, for it had previously been believed that it was so low that the reaction could be disregarded. It constitutes the first certain proof that simple alkyl radicals will isomerize by movement of a hydrogen atom even in the process of decomposition.

The problems of the bond strengths in acetone, acetaldehyde, and formaldehyde remain unresolved. There seems to be plenty of good evidence for each of the values that have been suggested, but it does not hang together.

For instance, kinetic evidence derived from several sources suggests that $D(H—CO) \leq 14$ kcal. mole$^{-1}$, whereas electron impact and photochemical threshold work leads to a value of some 27 kcal. mole$^{-1}$. The simplest way to produce acetyl radicals is by the photolysis of acetone or acetaldehyde. Radicals produced in this way may be "hot" and decompose more rapidly than radicals in thermal equilibrium with their environment. Calvert & Gruver (143) overcame this difficulty by photolyzing azomethane in the presence of acetaldehyde. Light of 3660 A was used which would not dissociate the aldehyde. The acetyl radicals were then produced by the reaction of methyl with the acetaldehyde. They found that the rate constant for the decomposition of acetyl to be given by

$$\log k/\text{sec.}^{-1} = 10.3 - (13500/2.3RT).$$

The rate constant for the reverse reaction was reported to be

$$\log k/\text{mole}^{-1}\,\text{cm.}^3\,\text{sec.}^{-1} = 8.2 - (3800/2.3RT).$$

Though the $A$ factors are lower than would normally have been expected, their ratio agrees well with that which can be calculated from the entropy change. Work on the photo-oxidation of ketones indicates, in keeping with previous work, that propionyl radicals are much less stable than acetyl.

Very little is known of the thermal decomposition of alkoxy radicals in the gas phase. McMillan & Wijnen (144) were able to obtain some information from the study of the photolysis of di-*t*-butyl peroxide and ethyl propionate. Only relative rate constants and activation energies could be measured. It was found that the loss of a methyl radical from *t*-butoxyl has an activation energy 3 kcal. mole$^{-1}$ higher than that of the abstraction of a hydrogen atom from the peroxide. The activation energy for the loss of a methyl radical from ethoxyl is 7 kcal. mole$^{-1}$ higher than that for the abstraction of a hydrogen atom from ethyl propionate (113).

## Biradicals

The purpose of this section is to discuss the reactions of substances such as methylene. It is arguable that the title is a misnomer, but no other word yet includes substances such as NH and oxygen atoms as well as the methylenes. One piece of work during the year tends to indicate that methylenes are, in fact, in the singlet state and do not contain unpaired electrons. Cvetanović & Sato have produced oxygen atoms by the photolysis of nitrogen dioxide (145) and by the mercury photosensitized decomposition of nitrous oxide (146). The second source, which has proved the more convenient, yields oxygen atoms in the ($^3$P) state (147). These atoms react with butenes to give epoxides and, by rearrangement, carbonyl compounds. The addition of an atom to *cis*-2-butene yields a mixture of *cis*- and *trans*-dimethyl ethylene oxides. This is interpreted as the result of an oxygen atom adding to a carbon atom at one end of the double bond to form a biradical. The two radical ends then combine to form the three-membered ring. The delay be-

tween the opening of the double bond and the closing of the ring is sufficient for internal rotation to occur. This behaviour is in marked contrast to that of methylene which adds to *cis*-2-butene to yield exclusively *cis*-dimethylcyclopropane. It may be argued that the former behaviour is typical of a true biradical, whereas the latter is typical of substances in a singlet ground state.

It is found that isobutene reacts about 5.5 times as fast as 1-butene with oxygen atoms from nitrous oxide. This is a much greater difference in reactivity than is found with methylene. Oxygen atoms preferentially attack the least highly substituted carbon atoms.

The study of biradical reactions in the gas phase is still in its infancy. One of the most important papers yet published on the subject is Frey & Kistiakowsky's (30) study of the reactions of methylene from the photolysis of ketene with ethylene, propane, cyclopropane, and *n*-butane. Methylene inserts itself across the C—H bonds of alkanes to yield the homologue with one more carbon atom. The attack on the various C—H bonds is nearly but not quite statistical, and the relative yields of products are almost independent of temperature. As has already been mentioned, methylene adds across the double bond of ethylene to yield a highly energized cyclopropane. If it is not rapidly deactivated, the cyclopropane will isomerize to propylene. Some propylene is always found in ketene-ethylene mixtures formed by the insertion reaction, but the amount of this reaction may be considerably reduced by the addition of inert gases. The inert gas apparently serves to deactivate methylenes that have been formed with excess energy.

Methylene will also abstract hydrogen atoms to yield methyl radicals. These radicals ultimately form products similar to those produced by normal biradical reactions. The methyl radical products can be almost eliminated if a small quantity of oxygen is added to the system.

The insertion reaction of methylene with cyclopropane yields activated methylcyclopropane, which at low pressures isomerizes to butenes. The pentenes formed by the isomerization of dimethylcyclopropane, from methylene and isobutene, are roughly in the proportions that their thermodynamic stabilities would indicate [Knox, Trotman-Dickenson & Wells (31)].

The range of unreactive gases that are available for investigations of biradicals is very limited. Kistiakowsky & Sauer (148) have found that sulphur hexafluoride reacts slowly with methylene and that carbon dioxide reacts 0.02 times as fast as ketene. It forms carbon monoxide and formaldehyde. Methylenes do not combine to give ethylene even at the high concentrations produced by flash photolysis.

### Oxidation

The study of low temperature oxidations remains a particularly British form of investigation. Considerable change does, however, seem to be apparent in the outlook of the investigators. For many years, studies of oxidations have been largely confined to the observation of the change of the total pres-

sure of the reactants with time, supplemented occasionally by analyses for a few of the very diverse products. The invention of gas chromatography has made it possible to determine a much larger number of products, 20 or more, in a reasonable time. Paper chromatography for the less volatile products is also being increasingly used. Thus, Taylor (149) has been able to detect several peroxides including hydrogen peroxide at many temperatures, but *t*-butyl hydroperoxide only at 250°C., in the oxidation of isobutane. Very sensitive detectors for gas chromatography have now been developed and it should soon be possible to investigate the very small amounts of products formed in the initial stages of the reaction, usually referred to as the induction period because little change in pressure takes place.

Detailed studies have been made of the oxidation of propylene (150), 1-butene (151), and 1-hexene (152) by conventional means. The reactions were carefully investigated under a wide variety of conditions, but no definite results that lend themselves to a summary were found. At the moment, we do not know enough to interpret all the effects. This applies also to a study of the combustion of cyclopentane by McGowan & Tipper (153, 154) and, to a lesser extent, to the study of the oxidation of ethanol (155). Amines have been found to inhibit oxidation when studied in the usual way, so Cullis & Waddington have investigated the oxidation of triethylamine (156) and trimethylamine (157). It is found that the amines markedly inhibit the further oxidation of the primary products. Dimethyl hydroxylamine, which is formed from trimethylamine, is a very efficient inhibitor. A complicated mechanism has been devised to account for observations on the oxidation of ethane by nitrous oxide between 530° and 670°C. (158).

Several investigations have been reported in which an attempt has been made to obtain more direct information on the elementary processes of oxidation. Burgess & Robb have investigated the mercury photosensitized oxidation of hydrogen (159) and several hydrocarbons (160) by following the rise in temperature of a platinum wire, stretched across the reaction vessel, owing to the rise in temperature that accompanies the exothermic reactions. It proved possible to obtain a considerable amount of fresh information on the elementary reactions, although the combination of hydrogen and oxygen must be one of the most studied systems in chemistry. Further information on the system was obtained by Forst & Giguère (161), who found that the second explosion limit of the oxidation was increased by the addition of hydrogen peroxide. In order to account for the quadratic dependence on the peroxide concentration they proposed that the steps:

$$H_2O_2 + H = H_2O + OH$$

and

$$H_2O_2 + OH = H_2O + HO_2$$

should be added to the generally accepted mechanism.

Burgess & Robb suggested that the rate determining steps of the chain

sequence in the oxidation of isobutane, isopropyl benzene, and cyclohexene were of the type:

$$RO_2 + RH = RO_2H + R.$$

On the other hand, reactions of the type:

$$RR'CHO_2 = RR'CO + OH$$

controlled the chain in the oxidation of *n*-pentane, *n*-hexane, and *n*-heptane. In each case the rate constant was measured. These results are extremely interesting but cannot yet be fully accepted, as they appear to conflict with other well-established findings.

In the absence of a complete knowledge of the systems, it would be useful to know the positions at which the chain-carrying radicals of oxidation attack the hydrocarbon molecules. 2-Methylpentanes have been prepared each of which is labelled at one carbon atom with $^{14}C$ [Cullis, Hardy & Turner (162)]. These compounds have been oxidized, and the activity of the carbon monoxide formed has been determined. Unfortunately, little information as to the point of attack can be deduced from such studies. Carbon monoxide is formed only after the original molecule has been attacked by a succession of radicals. A more direct approach is to measure the relative rates of consumption of, say, ethane and propane in a mixture [Knox, Smith & Trotman-Dickenson (163)]. It was found that the relative rates of consumption were independent of the composition of the mixture and the total pressure, as they should be if the rates are determined by the rate constants for the abstraction of hydrogen by the chain-carrying radicals. More surprisingly, the rates did not vary with temperature. The results were interpreted as consistent with an $HO_2$ chain. There are still many points that are not understood about even this simple finding. It seems likely that the nature of the chain reaction may alter considerably as the reaction progresses.

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# PHYSICAL AND CHEMICAL PROPERTIES OF SURFACES[1]

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*Physical adsorption.*—Among theoretical investigations, the work by Meyer (1) is of general interest. The author proposes the semiempirical isotherm equation: $P/(P_0-P)\theta = 1/C + (P/P_0)\ (1+\theta^2/k)$, $C$ and $k \approx \frac{1}{2} \ln C$, constant. For small and large $P$, this reduces, respectively, to the Langmuir and to the Frenkel-Halsey-Hill equations. It is pointed out that if the Brunauer-Emmett-Teller equation is applicable, the requirement $[P/(P_0-P)]_{v_m} = C^{-\frac{1}{2}}$ should be used as a check on internal consistency of the data. Meyer also suggests that the $v_m$ values calculated from the Brunauer-Emmett-Teller theory coincide with correct values only if $H_1 - H_1 \rightarrow RT$ as $\theta \rightarrow 1$. Apparently, this is the case for $N_2$ at 78°K., but the condition is not generally fulfilled; one should expect the calculated $v_m$ values to vary with temperature. Fisher & McMillan (2) derived a generalized isotherm equation, based on the assumption that the vibration frequency, $\omega$, varies as $\omega^2 \propto \theta^\gamma$ ($0 \leq \gamma \leq 1$). The crude Fowler-Guggenheim equation results as a special case of this treatment. Using order-disorder concepts, Bumble (3) has set up a systematic theory for localized, monomolecular adsorption on uniform surfaces. The Langmuir and the refined Fowler-Guggenheim equations arise as zero and first order cases; explicit calculations are provided for the second and third order cases, the latter taking into account interactions between next-nearest neighbors. Pace (4) has considered lateral intereactions and mobility in the outermost adlayer by utilizing a two-dimensional "lattice liquid" model, whose free volume is allowed to vary with $\theta$. From the partition function, the population of sites and other thermodynamic variables are derived; interactions between Ar and graphite are computed for various positions on the surface. Tykodi (5) has discussed seeming inconsistencies in thermodynamic variables as $\theta \rightarrow 0$; his arguments seem to lose much of their force, since they involve the incorrect assumption [e.g., Hill (6)] that Henry's law is incompatible with adsorption on heterogeneous surfaces. Schay, Fejes & Szathmáry (7) provide a theory for adsorption of mixtures of gases in a mobile adlayer. Dubinin, Zaverina & Timofeev (8) examined isotherms for 16 organic vapors on carbonaceous adsorbents and demonstrated the applicability of their own isotherm equation. Graham (9) has provided experimental proof that surface heterogeneity adversely affects two-dimensional condensation; this effect becomes more marked as lateral interactions are decreased.

[1] Material for this review was collected from publications received at the Chemistry and Physics Libraries of Purdue University between November 15, 1957 and November 15, 1958.

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The following adsorption studies have been carried out: isotherms for $N_2$ on various alumina gels are characterized by the same value of $C \approx 82G$ cal./mole in the Brunauer-Emmett-Teller equation; heats of sorption on various charcoals are generally greater because of porosity [Halász & Schay (10)]. $N_2$ isotherms on nonstoichiometric $WS_2$ catalysts have been reported by Samoilov & Rubinshtein (11). Ross & Pultz (12) report that BN exhibits a degree of uniformity comparable to that of carbons graphitized at 1800°C., as judged from adsorption studies of Ar and Xe. Isotherms of $CO_2$ and $NH_3$ on graphitized carbon blacks and heats of adsorption, determined by Spencer, Amberg & Beebe (13), are sensitive to residual oxygen and to homogeneity of the solid; the $NH_3$ isotherm is of type III. Despite the fact that adsorption isotherms of hydrocarbons, benzene, cyclohexane, $CCl_4$, $H_2O$, and $N_2$, on ammonium phosphomolybdate follow the Langmuir equation over most of the $P$ range, there is evidence for multilayer condensation in wide channels and in spaces between the crystallites; $NH_3$ penetrates the lattice [Gregg & Stock (14)]. The adsorption of mixtures of benzene, toluene, and xylene on active carbons has been studied by Iwakami (15). Isotherms of organic vapors on pyrex, determined by Bottomley & Reeves (16), demonstrate that allowance must be made for adsorption of gases on pyrex walls of containers in the accurate determination of virial coefficients. Interlamellar sorption processes on various types of clays have been described by Barrer & Reay (17). A review of Hungarian work in physical adsorption has been provided by Schay & co-workers (18).

The adsorption of water has been studied: On saran charcoals [Dacey, Clunie & Thomas (19)]; on active carbons, the isotherms changing markedly in the presence of oxygen [Dubinin & Zaverina (20)]; on glass, Cu, Ni, and alumina ceramics at very low pressures [Okamoto & Tuzi (21)]; on quartz and calcite [Hackerman & Hall (22)]; on $CaF_2$ [Amphlett (23)]; on vinyl polymers [Peterson (24)]; on lyophilized ribonuclease [Foss & Reyerson (25)]; and on wheat, desorption isotherms being analyzed according to an equation developed by the author [Becker (26)]. The sorption of $H_2O$ on silica gel has been studied by Kohlschütter & Kämpf (27), whose type IV isotherms diminish and exhibit a more pronounced hysteresis as the gel is heated to progressively higher temperatures; a decrease in $N_2$ surface areas occurred simultaneously. Zhdanov & Kiselev (28) noticed an increasing convexity of $H_2O$ isotherms toward the pressure axis as silica was heated to 650°C. in vacuum; the original properties of the adsorbent could be restored by rehydration.

In considering capillary condensation and hysteresis phenomena, Derjaguin (29) generalized the Kelvin equation so as to allow for the presence of adsorbed layers on the capillary walls; the general equation was applied to a variety of special cases. Arnell & McDermot (30) have examined causes for the wide prevalence of hysteresis in adsorption. From their scanning curves for butane, ethyl chloride, and ammonia on porous glass, Quinn & McIntosh (31) conclude that the "ink bottle" model holds and that some pores are

blocked by others. Dimensional changes of the adsorbent during adsorption are correlated with concave menisci of fluid, held in pores. Karnaukhov & Kiselev (32) consider the adsorbent as a system of regularly packed spheres and predict the onset of sorption hysteresis when the co-ordination number of the solid exceeds five. Holmes & Beebe (33) find that $NH_3$ on nonporous carbon black exhibits a pronounced hysteresis loop at $-78°C.$, whereas $N_2$ at $-195°C.$ does not; it is postulated that the graphitic crystallites undergo swelling in the presence of $NH_3$.

For surface area measurements, Vyroubal & Váhala (34) suggest the use of 2-anisole-azo-$\beta$-naphthol. Surface areas and particle size distributions for various metal powders and their oxides have been determined [Ehrlich & Schulze (35)]. Ar and He isotherms do not provide a true measure for the area of high rank coal [Kini, Ganguli & Lahiri (36)]. The pore structure and capillary distribution of active carbons has been examined [Turuizumi (37)]. The surface area of silica has been determined from gas adsorption, permeability, and microscopy studies [Cartwright, Wheatley & Sing (38)], and from benzene isotherms [Gärtner & Griessbach (39)]; surface properties and pore size distribution of kieselguhrs were determined from $N_2$ isotherms and by use of He [Jírů & Brüll (40)]. The area of alumina, prepared from aluminum isopropoxide, did not fall below 300 $M^2/g$ even after aging [Harris & Sing (41)]. Changes in the Brunauer-Emmett-Teller surface area of oxides with sample treatment have been investigated [Schwab & Marhenkel (42)]. In mixed $MgO-Cr_2O_3$ catalysts, the total surface area was obtained from sorption of $C_6H_6$, while the fraction due to magnesia was determined by chemisorption of $I_2$ [Rubinshtein, Afanasyev & Pribytkova (43)]. Surface properties of various silicates have been characterized [Noll, Kircher & Sybertz (44)]. Discrepancies in surface area measurements of siloxenes utilizing $N_2$, $Br_2$ and $CH_4$ [Kautsky & Pfleger (45)] can perhaps be ascribed to intercalation of $Br_2$ and of $CH_4$. The internal surface of clay minerals has been determined as function of temperature by use of Ar at 90°K. [Kirsch & Pruss (46)], and the porosity of natural minerals has been examined [Bykov, Gerasimov & Zalevsky (47)]. The total area and pore size distribution of solvent-exchanged cellulose fibers has also been reported [Thode, Swanson & Becher (48)].

Theories concerning adsorbent-adsorbate interactions are still under scrutiny. Constabaris & Halsey (49) applied the method developed by Steele & Halsey (50) to determine the interaction energy of Ar with graphitized carbon black. Freeman (51) refined this method by replacing the "hard sphere" repulsion potential in the integral for the apparent volume of the system, by an $r^{-9}$ repulsion potential. He correlated the method with the conventional thermodynamic analysis and investigated the effect of surface heterogeneity. Account was also taken of interactions between gas molecules; here, the pairwise additivity principle of potentials was shown to be inapplicable. Durham & Soderberg (52) have provided an elegant mathematical calculation of van der Waals interaction energies between $Cl^-$ ions

and NaCl at any position near the surface. In their method for calculating adsorption energies by summation over pairwise interaction potentials, Avgul, Kiselev & co-workers (53, 54) write out the attractive dispersion potential as a sum of terms in $r^{-6}$, $r^{-8}$, and $r^{-10}$; the repulsion constant is determined after summation of all interaction potentials, thereby reflecting the fact that a given surface group is in equilibrium with all atoms of the crystal. The adsorption energy for a complex molecule consisting of several centers (atoms, functional groups, hydrocarbon segments, etc.) is obtained by addition of the adsorption energies for the individual units; while this step is justified on the basis that dispersion energies are additive, it does require the assumption that each segment can accommodate itself on the surface in energetically favored positions, without straining the adsorbed molecule as a whole. Barrer (55) points out that calculated dispersion energies may be high because of the presence of lattice vacancies near the surface. Halász (56) cites expressions for differential heats of adsorption as a function of gas pressure.

Calorimetric measurements have been published for the following systems: Water vapor on NaCl; after an initial sorption, there occurs a decrease in surface without further adsorption, and water subsequently penetrates the lattice [Papée & Laidler (57)]. Benzene on alumina; observed entropies, $S$, agree best with a model involving two translational and one rotational degree of freedom in the plane of the ring. The value of $S$ first rises with $\theta$ to a maximum, due to increasing contributions from vibrational degrees of freedom normal to the surface, as the less energetic patches are filled, and then passes through a minimum, as clustering sets in [Gregg & Wheatley (58)]. $C_6H_6$, $n$–$C_6H_{14}$, and $n$–$C_7H_{16}$ on silica gels; the differential heats of adsorption together with isotherms show that the heats of adsorption increase sharply as the pores are narrowed. A sharp peak in the heats near the saturation vapor pressure is attributed to a sudden compression of liquid in the capillaries, as the concave menisci are flattened out prior to bulk condensation [Kiselev (59); Isirikian & Kiselev (60)]. $CH_3OH$, $C_6H_6$, and $n$-alkanes on quartz and silica gels; the standard heats of adsorption increase linearly with the number of C atoms of the adsorbate, and $\pi$ complexing contributes additionally to the adsorption energy of $C_6H_6$. Esterification of the silanol groups on the surface sharply decreases the adsorption energy of methanol because of the elimination of H-bonding [Kiselev (61), and Isirikyan & Kiselev (62); see also (217, 218)]. Rare gases on charcoal; $0.03 \leq \theta \leq 1$, the differential heats remain constant [Cremer & Gruber (63)]. Argon on graphon (a commercial grade of carbon black); on the homogeneous surface, the hump in the isosteric heat near $\theta = 1$ is very pronounced. Below 55°K., the heat capacity data indicate a transition, possibly from a mobile to a localized phase [Bobka, Dinniny, Siebert & Pace (64)]. He and Ne on graphitized carbon at 17°K.; the heat measurements at low coverage are interpreted in terms of a dual site model. Those at high coverage are interpreted on the basis of patchwise adsorption, each patch being under lateral compression.

Details of the proposed mechanism are still obscure [Aston & Greyson (65)]. For Ar, Kr, $N_2$, and $NH_3$ on graphite, the results compare favorably with calculations (53), after a dipolar interaction effect is included for $NH_3$ [Avgul & Kiselev (66)]. Benzene and *n*-alkanes on carbon blacks; various measured thermodynamic quantities are compared with theory (53). In almost all cases, the heats of adsorption increase linearly with the number of C atoms in the chain [Avgul, Kiselev & co-workers (67, 68, 69)]. Water vapor on wool keratin; the sorption is accompanied by clustering of water vapor on the surface and by swelling of the adsorbent [Morrison & Hanlan (70)].

Chackett & Tuck (71) calculated adsorption energies of Ne, Ar, Kr, and Xe on charcoals from their linear isotherms in the low pressure region. Juliš & Hodek (72) calculated thermodynamic quantities pertaining to the adsorption of $CS_2$ on "Winkler dust." In comparing differential heats of adsorption with dispersion energies calculated from theory, not all writers are aware of the difference in these two quantities. Rosenberg (73) has cited an interesting case concerning the adsorption of Kr on Ge; dispersion energies calculated by summation of pairwise interaction potentials is far greater than that calculated from the data. To obtain agreement, it is necessary to assume that a clean germanium surface is metalloid in character; this finding is in line with other indirect evidence (161) cited later.

Preliminary measurements on heats of immersion of anatase in water have been reported by Basford, Anderson, Murphy & Jura (74). Puri, Singh & Sharma (75) observed that the heat of immersion of charcoal in water changes with oxygen content; only oxygen liberated as $CO_2$ affects the measurements. The heat of wetting in organic liquid remains unaffected. A drastic decrease in the heats of immersion of graphon and graphite with increasing $\theta$ in benzene has been reported by Pierce, Mooi & Harris (76); this is presumably due to capillary condensation in interstices. The determination of free energies of immersion from the Gibbs equation, in conjunction with isotherms of $C_6H_6$, $C_6H_{12}$, $n$–$C_6H_{14}$, and $H_2O$ on silica gels has been discussed by Van Voorhis, Craig & Bartell (77); difficulties engendered by capillary condensation phenomena are also described.

Several interesting sidelines have been pursued: Using frontal gas chromatography, Fejes & Schay (78) have shown that the difference between intake and outflow of gas is a measure of its adsorption; isotherms of $N_2$ on charcoal at 20, 40 and 60°C., using $H_2$ as a carrier, were found to be linear. The same procedure was used by Schay, Székely & Szigetváry (79) to study adsorption of $CO_2$–$C_2H_2$ mixtures on charcoal. Gas chromatography was also used by Barrer & Hampton (80) to study the adsorption of $O_2$–Ar, $N_2$–Ar and mixtures of organic compounds on alkyl ammonium bentonites. Peters & Proksch (81) observed a marked change in the kinetics of desorption of Kr, $CH_4$, $C_2H_6$, and $C_3H_8$ from active charcoals near the critical temperature of each adsorbate; the utility of the phenomenon in the separation of gases is pointed out. A theory of thermodesorption has been provided by

Smith & Aranoff (82); the rise of pressure of gas into constant volume or into a vacuum leak is calculated under conditions where the adsorbent temperature rises linearly with time and where first or second order kinetics prevails. In connection with the production of ultra-high vacua, Bills & Carleton (83) have set up a theoretical study on the rate of adsorption of gases activated by electron impact.

*Chemisorption.*—A qualitative survey of the present status in this field has been provided by Schwab (84), and a book on the subject was published in 1957 [Garner (85)]. A generalized quantum mechanical treatment by Koutecký (86) shows that electrons are localized at the surface of a crystal if, on the energy scale, the distance of the new level from the nearest band edge is considerably greater than the band width. The chemisorptive bonds are essentially homopolar and interaction between chemisorbed atoms may occur via the electron cloud of the crystal. Tuck (87) has used Mulliken's theory of charge-transfer, no-bond complexes in conjunction with measured heats of adsorption of rare gases on charcoal, to compute numerical values for interaction integrals. The linear variation of heat of adsorption with polarizability of the adsorbates is due in part to their relatively high ionization potentials. Brodd (88) has used the same method to compute heats of adsorption of $H_2$, $O_2$, Cs, and Xe on a number of metals, after approximating interaction terms with numerical values accessible by experiment.

The application of the electron theory in ideal solids for interpretation of chemisorption phenomena continues to be under investigation. Garner (89) and Volkenshtein (90) have reviewed these concepts in terms of chemical terminology, with minimal reference to the band theory. Volkenshtein (91) regards adsorbed species on semiconductors in the same category as impurities. The chemisorption process and catalytic activity on solids is correlated with electronic bulk properties; the effects of light and of impurities are discussed. Other reviews are cited in articles dealing primarily with heterogeneous catalysis (see below). Some aspects of the boundary layer theory as applied to chemisorption processes have been criticized by Sandomirskii (92). A mathematical treatment of atomic or ionic adsorption in the presence and absence of space charge regions is presented by Krusemeyer & Thomas (93). Numerical calculations illustrating the effects of equilibrium between adsorbent and adsorbate and of the bulk and surface electronic states are provided.

Increasingly, the inadequacy of the simple band-structure model is becoming recognized. The attack is lead by Hickmott & Ehrlich (94) who ascribed the decrease in heats of adsorption with $\theta$ on metals to interactions between adatoms, although variations in binding energy are not completely discounted. In their lengthy article, they marshal evidence showing that chemisorption and desorption are sensitive to surface structure, and they criticize interpretations which invoke changes in surface dipole structure, or variations in the Fermi level to account for the observed effects. Their interpretations rest heavily on detailed kinetic measurements for the $N_2$–W,

$O_2$–W, and $H_2$–W systems; hence, their final conclusions cannot be accepted as decisively established. However, in support of these general ideas, the following work may be cited: Rudham & Stone (95) showed that their calorimetric heats of adsorption of $H_2$ on Co fell to a much greater extent than could be justified on the basis of mutual dipolar repulsions or penetration of charges into the double layer. They regard the steep initial slope of the differential heat curve as evidence for *a priori* heterogeneity. Two modes of hydrogen bonding are postulated; weak chemisorption bonds, involving *d* orbitals and more strongly bound states, involving hybridized orbitals. Klemperer & Stone (96) noted further that defects in unsintered Ni films contributed appreciably to the measured heats of chemisorption of various gases, and that some rearrangement in surface structure occurred during the initial stages of the sorption process. Mignolet (97) distinguishes two bonding states of $H_2$ on metals; these are interpreted in terms of the arrangement of sorption centers, which generally differs from that of the atoms in the crystal. In his view, a conversion from negative to positive surface films occurs when the site geometry allows two H atoms to come into close proximity, so as to permit strong interactions. Takaishi (98) likewise calls attention to heterogeneity effects in the chemisorption of $H_2$ on metals; he favors a bridge structure in which H is bonded to more than one site. In interpreting the chemisorption of $CO_2$ on 12 evaporated metallic films, Collins and Trapnell (99) were forced to take into consideration not only the band structure but also specific chemical factors. The above studies indicate the need of further refinement of our present theories of chemisorption.

The existence of several binding states has been stressed by Hickmott & Ehrlich (94), and the concept was used by Wolkenstein & Kogan (100) to explain photosorption phenomena. In their theory, the incident radiation generates hole-electron pairs, which cause a shift in the fraction of the weakly bound molecules; only the latter are presumed to be in equilibrium with the gas phase. Experiments on photosorption of oxygen in ZnO, by Solonitsyn (101), Fujita & Kwan (102), and Medved (103), are in general accord with this theory. A two-step mechanism is also cited by Kennedy, Ritchie & Mackenzie (104) in explaining their photosorption experiments of $O_2$ and of NO on $TiO_2$ films. Solonitsyn (105) observed that photosorption of $O_2$ on silica gel and crystalline quartz occurred when the incident wavelength was below 250 $m\mu$.

Chemisorption studies of gases on metals include the following systems: $H_2$ on Ni, Fe, Cr, and Pt in bulk and on films [Kavtaradze (106)]. $H_2$ on Ni films and Ni powder at $-196$°C.; the chemisorption process is hindered by impurities, but the physical adsorption of Ar or Kr remains unaffected [Roberts & Sykes (107)]. $N_2$, $O_2$, and CO an W; field emission micoscope experiments reveal several binding states [Ehrlich, Hickmott & Hudda (108)]. CO and $N_2$ desorbing from hot W filaments; chemisorbed oxygen is removed essentially as the oxide. This makes hot W a very efficient getter

for $O_2$ [Schlier (109)]. $O_2$ on Si films; the kinetics of adsorption and activation energy were determined in the range $10^{-4}$ to $10^{-2}$ mm. Hg [Law (110)]. Ethylene on evaporated Pd; the chemisorption at 0°C. is accompanied by decomposition [Stephens (111)]. $O_2$ on various metals, after exposure to a discharge [Low (112)]. The chemisorption heats of $H_2$ on metals have been shown to be a periodic function of the position of the elements in the periodic table [Kavtaradze (113)].

The adsorption of water vapor on alumina, MgO, $ThO_2$, and $SiO_2$, has been studied by Oblad, Weller & Mills (114); their attempts to introduce strains into the oxide catalysts by dehydration at high temperatures failed because an annealing process occurred at the same time. Tuzi & Okamoto (115) have reported on the chemisorption of ethylene and of $O_2$ on BaO films in the range 23–105°C. McConnell (116) used a "cyclone mircronizer" for producing solid solutions of oxides; the heats of chemisorption of oxygen on $UO_2$–$ThO_2$ mixtures varied with composition.

The chemisorption of CO below 500°C. on graphite results in the deposition of C; no $CO_2$ is produced. It is postulated that $C_3O_2$ is formed as an intermediate by the complexing of two CO molecules at one site [Deitz & Prosen (117)]. The rates of sorption of $O_2$ and the rates of desorption of the products CO and $CO_2$ from graphite obey the Elovich equation [Bonnetain, Duval & Letort (118)]. The role of surface hydroxyl groups on silica gel, porous glass, or quartz has been studied by Bastick (119), who finds that the relative $N_2$ isotherms on various gels superpose, while those of $NH_3$ do not; this indicates chemical binding of ammonia. Soboleva & Kiselev (120) observe that methanol is hydrogen bonded to the surface so that methylation or dehydration alters the sorption process. de Boer and Vleeskens (121) have studied the dehydration process in silica in detail and conclude that residual OH groups remain on the surface; this is borne out in other work cited below. Papee (122) has studied the sorption of water, rehydration, and transformation of various activated aluminas.

Regarding solid catalysts, Leibowitz, Low & Taylor (123) report that the rates of $H_2$ chemisorption on nickel-kieselguhr samples follow the Elovich equation. The results are treated in terms of the Taylor-Thon mechanism of site generation; however, other mechanisms also yield the same rate law. The rate of chemisorption of CO on $MnO_2$ has been investigated by Elovitch (124). Kiperman, Balandin & Davydova (125) cite a value of 57.1–57.9 kcal./mole as the binding energy of oxygen to their nickel catalysts. Kokes & Emmett (126) observed appreciable chemisorption of $N_2$ at −195°C. on nickel catalysts prepared from NiO; the $N_2$ could be recovered at room temperature. MacIver, Emmett & Frank (127) have reported on the chemisorption of various alkanes on silica, alumina, and silica-alumina catalysts. The sorption of $N_2$ on ammonia synthesis catalysts has been examined in detail by Scholten & Zwietering (128); their experimental work on bulk material differs from that of Greenhalgh, Slack & Trapnell (129) on films. They also criticize interpretations in publications on this subject by Horiuchi

& Kita (130) and by Kwan (131). In a reply, Kwan (132) states that for any single run, his own rate equation provides a better fit for the experimental data; although in a series of experiments, the Elovich equation reproduces the totality of the data equally well.

*Heterogeneous catalysis and electronic properties of catalysts.*[3]—There is continuing interest in the relation between the electronic properties of solids and their catalytic activity. Reviews of the current status in this field have been provided by Dowden (133), Hauffe (134), Volkenshtein (135, 136), Roginskii (137), Schuit & van Reijen (138), and Rienäcker (139). Winter (140) has demonstrated the utility of isotope exchange experiments in the study of this problem. The influence of crystal face geometry on catalytic action has been summarized by Gwathmey & Cunningham (141). While it is generally emphasized that electronic properties of solids are a primary factor in determining their catalytic activity, it is also pointed out that correlations should be drawn up with great care. There are many cases where a simple interpretation is not possible; for example, Roginskii (137) notes that $p(n)$ type materials are not necessarily the best catalysts for reactions involving electron transfer to (from) the solid. It is further demonstrated (139) that any disorder in solids significantly affects the reactivity of a given catalyst [compare also (96)]. In this connection, Liashenko and Stepko (142) state that measurements of the work function provide a more direct insight in the relation between electronic surface states and catalytic activity than measurements of conductivity.

These comments are reflected in discussions of specific experimental situations pertaining to metals, alloys, and elemental semiconductors: in the hydrogenation of $CO_2$, there is a progressive changeover in product from $CH_4$ to CO as nickel is alloyed with increasing quantities of copper; this is paralleled by a sharp drop in the Curie point [Cratty & Russell (143)]. On the other hand, the specific activity and activation energies for the hydrogenation of benzene over Ni-Cu alloys do not change in a simple manner with composition [Hall & Emmett (144)]. In particular, there is no sudden alteration at the critical alloy composition, where the *d* band is just filled. It is suggested that complications arise because the frequency factor itself is very sensitive to changes in activation energy. The oxidation of CO is characterized by an activation energy that is less for the 95–5 alloy of Ag–Pd than for either of the pure components. It is assumed that oxygen forms somewhat heteropolar bonds and hence, is primarily held on Ag, where electrons in the 5*s* band are available; CO is assumed to form a more nearly covalent bond and to be held preferentially on Pd metal, where the *d* shell is not completely filled [Schwab & Gossner (145)]. In the classic work by Couper & Eley (146), the activation energy for *para* hydrogen conversion increased sharply precisely at the alloy composition where the *d* band becomes completely filled. In continuing this work, Eley & Luetic

[3] Due to space limitations, only a very restricted part of the field of heterogeneous catalysis can be taken up here.

(147) find that in the decomposition of formic acid, the activation energy increased before this critical alloy composition was reached; a two-site mechanism seems to be involved in this reaction, thereby increasing the requirement for holes near the surface.

Clopp & Parravano (148) find that the decomposition of $H_2O_2$ is sensitive to changes in electronic structure in Bi and Sb, induced by alloying; this is particularly true of Bi, where the Brillouin zone is almost completely filled. On the other hand, the reaction was not greatly affected by a changeover from *p* to *n* type behavior in Sb alloys, showing again that the electronic conduction of the bulk material is not a reliable criterion for predicting catalytic properties. The authors also warn very strongly against construction of a general theory of catalysis based on results available to date. The hydrogenation of ethylene and the dehydrogenation of formic acid and of ethanol over Ge, Si, In, Sb, InAs, and AlSb has been studied by Schwab, Greger, Krawczynski & Penzkofer (149). In almost all cases, the apparent activation energy is greater on *p* than on *n* type semiconductors; however, the authors point out the difficulties in making quantitative correlations. Schwab, Block, Müller & Schultze (150) have explained their observed rates of reduction and activation energies for dehydrogenation of formic acid on intermetallic compounds such as $CuMg_2$, $Cu_2Mg$, and AgMg, as due to the formation of MgO which, in turn, creates electronic repercussions in the solid.

Concerning oxidic semiconductors, an anomaly was noted by Cimino, Molinari & Romeo (151) in the oxidation of CO and in the decomposition of $N_2O$ on NiO, as the temperature of the catalyst passed the antiferromagnetic transition point; the resistivity and thermoelectric power changed, and the chemisorption of oxygen on this oxide similarly suffered anomalies at the transition temperature. The enhanced catalytic activity is ascribed to a temporary increase in *p*-type character of the oxide. Keier, Roginskii & Sazonova (152) have verified that there is a close parallelism between the oxidation of CO on NiO and the electronic bulk properties of the solid. Upon varying the *p*-type character of this oxide by admixture of altervalent ionic impurities, both the frequency factor and the activation energies were altered. In a study of the oxidation or dehydrogenation of alcohols on ZnO, Myasnikov (153, 154) has established a linear correlation between catalytic activity of the oxide and its conductivity, which was altered by changing the partial oxygen pressure in the gas phase. He traced the effect of irradiation to the formation of excited $O_2$ molecules on the surface [see also (100)]. On the other hand, Rohmer, Avrillon & Hiss (155) emphasized that factors such as sample preparation must be taken into account in judging the effectiveness of ZnO in the catalytic decomposition of $N_2O$; this matter is documented in some detail. Szabó, Solymosi & Batta (156) observed that formic acid was subject to dehydrogenation on ZnO and to dehydration on $Al_2O_3$ and $TiO_2$. On NiO this reaction was characterized by a very low activation energy, and the surface regions were found to be partially reduced;

the addition of altervalent impurities was found to have a marked effect. García de la Banda & Marín (157) have investigated the electrical conductivity and activity of $ZnO$–$Cr_2O_3$–$KCrO_4$ catalysts with respect to the decomposition of isopropyl alcohol. A rough correlation between electric conductivity and catalytic activity was noted. Tucker & Gibbs (158) have carried out an interesting experiment, in observing that the decomposition of $H_2O_2$ on alumina contaminated with $Mg(NO_3)_2$, is facilitated on those locations where a high dislocation density was encountered. Such dislocations can warp the energy surfaces in a manner either favorable or unfavorable for the catalytic reaction of interest. This type of experiment shows very clearly the necessity of taking into account not only the electronic bulk properties of the material but also changes in such properties, induced by perturbations of the surface.

Turkevich & Laroche (159) have used electron paramagnetic resonance as a means of detecting free electron spins on charcoals; those heated to 650°C. show the greatest number of free spins and the least degree of interaction and localization of the surface electrons. They were also characterized by the highest activity with respect to *para* hydrogen conversion at −195°C. and by the least degree of activity with respect to hydrogen-deuterium exchange at 50°C. The reverse was true of charcoals heated to 950°C., which were found to possess a limited number of strongly interacting electrons. These findings are entirely in accord with expectation. Along similar lines, Donnet & Henrich (160) have found that certain types of carbon blacks interact strongly with free radicals and drastically inhibit free radical polymerization processes, indicating the presence of unpaired electron spins in surface regions. In another important experiment, involving sputtered films of Ge, Sandler (161) reports *para* hydrogen conversion, proceeding by a magnetic spin inversion mechanism. The data indicate the presence of approximately one unpaired electron spin per surface atom; a chemical inversion was ruled out by the absence of H–D exchange. These conclusions are in accord with findings described earlier (73).

*Adsorbent-adsorbate interactions.*—A systematic review concerning the effect of adsorbed gases on physical properties of solids has been published by Moesta (162). Kisliuk (163) has developed a theory for calculating the sticking probability of gas as a function of $\theta$ in terms of one parameter. Despite oversimplifications of which the writer is aware, his treatment seems physically more reasonable than prior derivations. Accommodation coefficients for removal of O atoms from the surface of 28 materials have been measured by Greaves & Linnett (164). The valency induction experiments of Selwood have been continued by Matsunaga (165); using iodometric titration and magnetic susceptibility measurements, he showed that the mean oxidation number of chromium dispersed as oxide on alumina or ZnO fell from 6 to 3.5 as the weight percentage of chromium increased from 0 to 28 per cent in samples heated from 300 to 450°C.; a structural rearrangement was noted in the temperature range of 300–350°C. These experiments are

of interest in connection with polymerization catalysts. Expansion-contraction effects during adsorption have been studied by Folman & Yates (166), who note that with increasing coverage of porous glass by polar gases there is first an expansion, then a contraction, then a further expansion. The contraction effects are ascribed to the presence of two different types of adsorption sites on the surface. The extensions of carbon rods exposed to a wide variety of gases have been determined as a function of pressure by Flood & Lakhanpal (167); these data are successfully interpreted in terms of adsorbent and adsorbate stress intensities, calculated on the assumption that the adsorbate acts as a single component complex. Forestier (168) has reviewed the very marked effect of gases, including those considered chemically inert, on reactions in the solid state, on fusion, phase transformation, mechanical surface properties, and the like.

Gebhardt & Herrington (169) claim that discoloration in $TiO_2$ subjected to heating in vacuum is due to the presence of organic impurities which partially reduce the surface region; this effect is not observed in the absence of such impurities. Rosenberg, Robinson & Gatos (170) found that during thermal restoration of oxygenated germanium, oxygen is discharged as the volatile oxide GeO, and that a rearrangement in the surface exposes more Ge to the ambient. Similar conclusions were reached by Dell (171), who finds that an oxygenated germanium surface is permanently altered on sintering in $H_2$ between 600° and 850°C. Contrary to the work by Law (172), Dell does not observe chemisorption of $H_2$ and CO at room temperature on germanium prepared by reduction of $GeO_2$; the differences may be due to differences in sample preparation. Dell further observed a logarithmic rate law for chemisorption of $O_2$ at 25°C.; the *p*- or *n*-type character of germanium had little effect on the extent of oxygen chemisorption because, near room temperature, the element is an intrinsic semiconductor.

The marked changes in work function or contact potentials due to adsorbed surface layers are under continued investigation. Work on metals is reported by Morgulis & Gavriliuk (173), Dykman (174), and by Culver, Pritchard & Tompkins (175), who describe the use of a space charge limited diode for this purpose. The effect of CO and $N_2$ on W has been studied by Eisinger (176). Very careful measurements have been reported by Dillon & Farnsworth (177) for $H_2$, $N_2$, and $O_2$ on Si, prepared by the floating zone technique, and by Fowler (178) for $O_2$ sorbed on graphite.

Mignolet's general concepts (97) have received further support by two sets of meticulous experiments, involving the interaction of $H_2$ with evaporated Pt films [Suhrmann, Wedler & Gentsch (179)] and with evaporated Ni films [Sachtler & Dorgelo (180)]. The changes in conductivity, $\sigma$, and emission of photoelectrons (Pt films only) upon chemisorption of $H_2$ at very low pressures indicate that $H^-$ is formed initially and that $H_2^+$ is present at greater surface coverage. As the temperature is raised, an increasing fraction of the chemisorbed species dissociates into protons and electrons, and diffusion into the interior competes with establishment of the firmly

bound species. Suhrmann, Wedler & Krüger (181) conclude from resistivity studies of Ni covered with $C_6H_6$, that the *pi* electrons of the aromatic compound are involved in the binding [compare also (61, 62)]. Changes in $\sigma$ with adsorption have also been determined for the system $H_2$–ZnO [Myasnikov (182)] and for $O_2$, CO, $CO_2$, $H_2O$, $C_2H_6$, and $C_6H_6$ on $MnO_2$ [Elovich & Margolis (183)]; here the interpretation is complicated by variations in the stoichiometry of the oxides, by changes in the method of sample preparation, and by the presence of impurities. According to Voltz & Weller (184), the conductivity of silica alumina catalysts in the presence of $NH_3$, menthyl-, dimethyl-, or ethyl amines, varies with the type and pretreatment of the catalyst. The authors believe the current carriers to be $NH_4^+$ ions or protons which are readily shifted from one amino group onto another.

Magnetic studies have been used as another criterion of solid-gas interactions. Gray & McCain (185), in investigating the susceptibility of Pt as a function of oxygen uptake at elevated temperatures, found that the initial state could not be restored except by treatment in $H_2$. The data conform to Pauli's theory of paramagnetism; each sorbed oxygen is believed to immobilize electrons on 50 neighboring Pt atoms. Vaska & Selwood (186) have reported a continuing, slow uptake of $H_2$ by Ni supported on silica. This process, which ceases only at pressures of 100 atm., is accompanied by a continuous decrease in magnetization of the samples. Selwood (187) describes the use of a low frequency AC permeameter for magnetization measurements. Earlier results obtained with $N_2$ on supported Ni are revised; it is found that relative to $H_2$, the change of magnetization with $N_2$ is small; $N_2$, Kr, and Ar are physically adsorbed.

Other types of solid-gas interactions have been reported as follows: the influence of adsorbed BaO layers on the photoelectric emission of a Cs–Sb cathode [Gavriliuk (188)]; the effects of ambient on the surface photocurrent in anthracene, where electron acceptors increase while electron donors decrease the photocurrent [Waddington & Schneider (189)]; the effect of $I_2$ on the reflection spectrum of $\gamma$ AgI [Nikitine & Perny (190)]; the influence of gases on the luminescence of ZnO [Tagantsev & Terenin (191)]; and the effect of $H_2O$ on the fluorescence of natural minerals [Przibram (192)]; the utilization of preferential adsorption on alumina at 20.4°K. to separate *ortho* and *para* hydrogen and to enrich *para* deuterium [Cunningham, Chapin & Johnston (193)]; the ionization of Na by hot W [Romanov & Starodubtsev (194)]; the ionization of K, KCl, and CsCl on W filaments in the presence of strong electric fields [Zandberg (195)]; the effect of patches on surface ionization phenomena in W [Zemel (196)]; the ionization of electronegative gases and of K, and the mobility of K on hot Pt [Moesta (197)]; the modification of the equilibrium profile of Ge and Cr surfaces in the presence of oxygen [Bénard, Moreau & Grønlund (198), Moreau (199)]; the electroviscous effect in carbon blacks [Donnet & Reitzer (200)]; the passage of $Li^+$ through evaporated layers of Al [Beliakova & Mittsev (201)]; and the kinetics of interaction between gases and metallic surfaces, on the

basis of collision theory, allowing for replenishment of active centers by atomic diffusion [Arslambekov (202)]. An experimental study on the energy exchange between cold gas molecules and graphite has been reported by Meyer & Gomer (203).

*Properties of adsorbed layers.*—In a very fundamental study, Derjaguin & Zorin (204) have examined the condensation of vapors on polished glass in elliptically polarized light. Near the saturation vapor pressure, nonpolar adsorbates changed smoothly from multilayer adsorption to bulk condensation, while adsorption of polar gases was limited to several layers, and bulk condensation occurred only subsequent to a phase transformation. Apparently, the adsorbed polar film is oriented in a manner dictated by the surface, and a transition to the liquid structure precedes condensation. It would be of interest to determine whether similar effects are noted on other surfaces.

Considerable work on spectra has been reported. This includes a study on the K absorption spectra of cobalt compounds sorbed on magnesia; the spectra differ from those of cobalt salts in a displacement of the cutoff toward shorter wavelength, and in the fine structure near the cutoff. Mixtures of magnesia and cobalt salts yielded patterns characteristic of the individual components [Sakellaridis (205)]. The nuclear magnetic resonance spectra of water sorbed on solids has been investigated from a theoretical viewpoint by Miyake (206). Measurements for water adsorbed on silica gel by Zimmerman & Lasater (207) led to evidence for the existence of two binding states; the fraction of the tightly bound component approaches 0.62 at high coverage. Lifetimes and nuclear correlation times of the adsorbate were also estimated. A break in the latter occurs at the onset of the second phase and again when the first monolayer is complete; this yields an independent check on the quantity $v_m$ of the Brunauer-Emmett-Teller equation. Graham & Phillips (208) report that *n*-heptane adsorbed on carbon surfaces in less than monolayer amounts exhibits a broad resonance spectrum, indicative of the absence of free rotation. Various alcohols on the surface display the typical $-CH_3$, $-CH_2$ and OH proton lines, all displaced to the same extent towards lower frequencies. It is suggested that such shifts are indicative of the presence of unpaired electrons in the surface regions of the solid, and that this shift is a convenient means of detecting such electrons. Erb, Motchane & Uebersfeld (209) have carried out very sophisticated experiments in saturating the electron spin system of carbon and observing an enhanced nuclear magnetic resonance of protons in adsorbed hydrocarbons, $C_6H_6$, $NH_3$, and $H_2S$. This yields new evidence concerning the interaction of the adsorbate with the free electron spins of the substrate. Hirota & co-workers (210) noted that the acidic proton signal disappeared when formic acid was adsorbed on silica gel, and that the proton attached to the carbon exhibited a very broad resonance line. These experiments demonstrate again, if further proof were needed, that nuclear magnetic resonance and electron paramagnetic resonance studies are powerful tools in the investigation of surface phenomena.

Further insight concerning the nature of the sorption process can be gained from infrared spectra. This matter is discussed in two recent review articles [Eischens (211) and Eischens & Pliskin (212)]. Yang & Garland (213) distinguish between several binding states of CO molecules attached to Rh on the surface; the reaction of these surface groups with $O_2$, $H_2$ and $H_2O$ has also been followed spectroscopically. From changes in the adsorption spectra of various aromatic compounds on $SiO_2$ and AgI, Karagounis & Peter (214) obtained information on electronic perturbations of the adsorbate by the adsorbent. Yates and Sheppard (215) deduce from the presence of normally inactive bands, that on the surface of porous glass, the simpler alkanes show an induced asymmetry. From the lack of resolution of the P and R branches of $CH_4$, it appears that this molecule may rotate only about an axis normal to the surface. The electric field near the surface is estimated at $7\times10^6$ v./cm. Price, Sherman & Wilkinson (216) have examined the spectra of water adsorbed on various alkali halides in detail. Infrared spectra for formic acid adsorbed on silica [Hirota *et al.* (210)] show that no ionization or dimerization occurs. Changes in the surface structure of silica on dehydration have been studied by McDonald (217) and by Young (218); infrared studies show that residual silanol groups remain even after strong heating, and that partial rehydration could be effected by exposure to water. $H_2O$ isotherms (218) conform reasonably well to those cited earlier (28, 119); there is over-all agreement on the principal properties of this system (120, 121).

Further information regarding the silica gel-water system was obtained by Kämpf & Kohlschütter (219), who studied variations in the real and imaginary parts of the complex dielectric constant as a function of frequency and of $\theta$. As all workers on this problem do, these authors distinguish between tightly and weakly bound molecules of water. Electrical properties of ethanol adsorbed on alumina gel have been studied by Shimizu (220). The Debye dispersion of sorbed water has been determined by Zhilenov (221), who noted changes in the temperature dependence of the dielectric response at the onset of capillary condensation; the activation energies for polarization and for electric conductivity exhibited a break near $-100$°C., which is indicative of a phase change.

Further insight concerning the behavior of sorbed molecules is afforded by the beautiful field emission experiments of Gomer and his school. The surface diffusion of CO and of inert gases on W has been repeatedly investigated by Gomer (222); the adsorption and diffusion of $O_2$ on W has been studied in detail by Gomer & Hulm (223), and the system $H_2$–Ni has been examined by Wortman, Gomer & Lundy (224). Ehrlich, Hickmott & Hudda (225) report on the interaction of Ar, Kr, and Xe with W. These techniques, if carried through a wide temperature range, afford a direct view of sorption and diffusion processes; it is also possible to determine changes in work function during adsorption, effects of various crystallographic planes on the surface processes, onset of aggregation of the adsorbate into crystallites, activation energies for various processes, and extent of

surface heterogeneity. Among many interesting phenomena, it may be mentioned that rare gases tend to retain their liquidlike structure well below the bulk melting point, and that after completion of a fourth layer, nucleation of "gas crystallites" takes place. This latter observation is reminiscent of work mentioned earlier (204).

Diffusion of adsorbed molecules has been discussed by Babbitt (226). Surface diffusion experiments have been carried out by Haul & Peerbooms (227), and by Habgood (228) in conjunction with molecular sieve action; in both cases, the diffusion coefficient $D$ passes through a maximum with increasing $\theta$. Habgood observed that for mixtures of $N_2$ and $CH_4$, the data cannot be fitted over the entire range except by use of negative $D$ values. To overcome this difficulty, the author suggests that diffusion is controlled not by the concentration gradient but by the gradient of chemical potential. The mathematical analysis indicates that $D$ should vary roughly as $1/(1-\theta)$, as is approximately the case.

The density of water adsorbed on montmorillonite has been investigated by Mackenzie (229) and the deposition patterns of glycerol aerosol impinging on coated microscope slides have been studied by Gallily & La Mer (230).

*Physical properties of surface layers and thin films.*—General reviews of this field are provided in two recent publications [Wolf (231), Auwärter (232)]. Quantum mechanical calculations [Koutecký (233)] show that metallic electrons are localized near the surface of a crystal. The number and distribution of the corresponding energy levels depends on the depth of penetration of the perturbation potential. Wave functions for "subsurface states" attain a maximum at some distance below the surface. A general formula for the surface energy has been given by Bertaut (234); troublesome infinities in ionic lattices are ascribed to volume polarization. Brunauer (235) reviews experimental data on finely divided solids in terms of surface enthalpy and energy concepts. The thermodynamics of curved surfaces has been reviewed by Guggenheim (236); the surface tension of several metals has been computed by McLachlan (237). Interfacial free energy calculations are presented by Cahn & Hilliard (238); Adam & Livingston (239) clarify concepts relating to contact angles and to work of adhesion. Prior derivations of the Gibbs adsorption relation have been criticized, and an extension of Thomson's relations has been provided by de Witte (240).

Methods for preparing scrupulously clean surfaces of metals and semiconductors have been described by Wolsky (241) and by Farnsworth & co-workers (242); the latter group reports a displacement of surface atoms relative to those in the bulk. Ling (243) has analyzed distributions of surface roughness on metals. Electron microscopy has been repeatedly used to study the surface structure of various metals and alloys [Chatterjee (244), Tsuchikura & Ichige (245), and Takashaki & Ashinuma (246)].

Electromagnetic properties of thin layers have been investigated repeatedly, for comparison with those for bulk materials, for ascertaining the effect of changing film thickness, and for the detection of changes in

film structure. The conductivity, $\sigma$, and the Curie point of thin Ni films has been determined as a function of film thickness by Colombani & Goureaux (247, 248). Low frequency AC current has been utilized to measure the Hall coefficient, $R_h$, of Ni deposits; an inversion of sign in $R_h$ occurs in very thin films; the magnetization saturation measurements indicate a reorientation of domains [Goureaux, Huet & Colombani (249)]. Magnetoelectric properties of Ni films subjected to magnetization saturation have been reported by Rappeneau (250). The variation of coercive field with angle relative to the Ni film was measured by van Itterbeek & Dupré (251). The thermoelectric power, $Q$, of cobalt passes through a maximum as the film thickness is increased; $\sigma$ and $Q$ vary with pretreatment of the sample [Savornin (252)]. Ferromagnetic properties of Co layers have been investigated by Reimer (253); Co deposits on Cu initially assume a cubic and not a hexagonal configuration, in mimicry of the underlying support. According to Uny & Nifontoff (254), the resistance of silver dispersed on amorphous silica varies with current and time. The influence of Se on the resistivity of Au is discussed by Minn & Damany (255). Colombani, Huet & Vautier (256) have given a brief account on the magnetoresistance, $R_m$, in thin films of Sb and Bi.

Reimer (257) reports a marked change in $\sigma$ after annealing an amorphous layer of Ge at 300°C. Barnes & Banbury (258) describe electrical properties of Ge 111 crystal faces cleaved by magnetically operated levers. From studies of $\sigma$, $R_h$, and $R_m$, Zemel & Petritz (259) conclude that the energy band structure of bulk Ge also carries over to the space-charge region near the surface; two types of holes and one type of electron have been detected. Millea & Hall (260) have verified that carriers arriving at the surface of Ge and Si are not scattered with equal probability into any solid angle. Intermetallic III–V element combinations seem to be extremely sensitive to the degree of order in thin films. Günther (261) heated the components separately and allowed these to impinge on a receiver plate maintained at elevated temperatures. Large variations in $\sigma$ and $R_h$ were achieved by altering the conditions for deposition. Paparoditis (262) correlates a minimum in $\sigma$ and $R_h$ for thin layers of InSb with the ordered stoichiometric composition of the film, annealed in the range 230–280°C.; powder patterns reveal the presence of constituent metals in untreated samples or in films annealed at higher temperatures. Likewise, Reimer (263) has noted a drastic change in $R_h$ and in $R_m$, as InSb films are made stoichiometric by heating to 400°C. With increasing film thickness $R_h$ is reduced, due to random deposition of the higher layers. A theoretical interpretation of electrical measurements on thin InSb films is discussed by Columbani & Launay (264). Ishiguro, Sasaki, Arai & Imai (265) report on a very comprehensive series of experiments in which they utilize conductivity, Hall effect, thermoelectric power, photoconductivity, transmission and reflection, and multiple beam interference studies to characterize electrical properties of $SnO_2$ films, evaporated onto quartz, glass, and rock salts. Surface photoconductivity studies for thin CdS layers subjected to a magnetic field are reported by

Tanaka & Masumi (266) and the electric breakdown in such layers has been studied by Böer, Kümmel & Misselwitz (267).

Bremer & Newhouse (268) have described thermal propagation effects when thin Sn layers return from the superconductive to the normal state. The remanent magnetization of thin NiO films has been determined by Yamaguchi (269), who utilized electron diffraction patterns. Employing penetrating electron beams and beams at grazing incidence, the author (270) detected differences in composition of $ZnCr_2O_4$–ZnO, Cu–NiO, and $Al_2O_3$–Pt catalysts on the surface relative to the interior regions.

X-ray studies or electron diffraction experiments have been done for metal films condensed on glass [Rieser (271)]; on thin films of V [Agarwal & Givens (272)]; on layers of $Sb_2S_3$, containing small amounts of $Sb_2O_3$ as a result of air oxidation [Vertsner, Gorbunov & Oksman (273)]; on Bi and various alkali halides [Queisser (274)]; and on $Eu_2(SO_4)_3 \cdot 8H_2O$, where the finely divided specimens exhibited at least two lines not present in the absorption spectrum of single crystals [Jura & Nathans (275)]. The following types of optical measurements are reported: The color technology of white surfaces [Hunter (276)]; measurements of optical constants of thin dielectric films by means of frustrated total reflection [Sanford (277)]; the transmission and reflection of visible light for thin silver films, as affected by the atmosphere [Trompette (278, 279)]; optical constants for evaporated Cr films [Hill & Weaver (280)]; optical properties of evaporated $CeO_2$ layers [Hass, Ramsey & Thun (281)]; the usefulness of SiO and ZnO as antireflection coatings on Ge and Si [Cox & Hass (282)]; and the use of interference colors for determination of thickness, and dielectric constant of thin anodic films on tantalum [Young (283)].

The electrochemical behavior of silver films has been elucidated by Trümpler & Hintermann (284). Heats of sublimation of zinc, and surface free energies have been determined through mass spectrometric studies [Poltorak & Panasuk (285)]. Lavine, Rosenberg & Gatos (286) have shown that different crystal faces of InSb undergo oxidation at different rates. The friction and durability of films on stainless steel has been investigated by Cottington & co-workers (287); the surface reorientation on metals caused by abrasion is reported by Scott & Wilman (288). Lindegaard-Andersen (289) has studied the plastic deformation in zinc oxide films, and Welch (290) reports on surface hardening of nonferrous metals by spark discharge.

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# BLOCK AND GRAFT COPOLYMERS[1]

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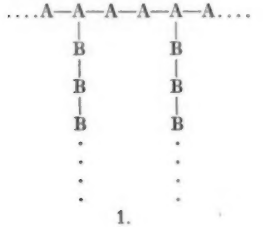
The volume of literature devoted to the investigation of polymeric systems continues to grow at such a great pace that it is no longer possible to review the whole of the available field in sufficient detail and sufficiently critically. Consequently, as in the past, a specific corner of the field has been selected for treatment. Even so it has been necessary to exclude polymers of regular structure and polymers containing blocks of regular and random structure, despite the obvious interest which is attached to such materials (1).

As well as the normal papers published during the year, the proceedings of the highly successful High Polymer Symposium held in Prague in September 1957 have been published (2, 3). Books on polymerization kinetics (4) and solution properties (5) by eminent authors have been published in the past year.

The production of copolymers of nonrandom structure was first proposed by Mark (6) and has achieved considerable significance both from a technical and academic point of view. Technically, such polymers are of importance because of the wide range of new physical properties to which they can give rise and, academically, the problem of their production and purification and the study of their solution properties has been the subject of much thought and work. Graft copolymers are branched macromolecules in which the branches are of a different type from the backbone 1.; block copolymers are linear macromolecules containing long sequences of units of differing types 2.



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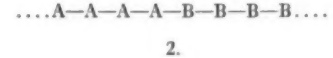


2.

## Synthesis of Graft Copolymers

*Radical attack on preformed polymer.*—If polymerization of a vinyl monomer is carried out in the presence of a preformed polymer of a different monomer, it might reasonably be expected that the propagating macroradical could abstract from the polymeric molecule a hydrogen (or other)

[1] The survey of the literature was completed September 1958.

atom, thereby transferring the radical character to the foreign polymer. Since (subject to steric considerations) abstraction can take place anywhere on the polymer molecule, the position of the free electron may be anywhere on the chain. This radical then can induce polymerization of the monomer giving rise to the required branch chain structure. Thus

$$\ldots\text{A—A}\cdot + \ldots\text{B—B—B—B—B}\ldots \rightarrow \ldots\text{A—A} + \ldots\text{B—B—}\dot{\text{B}}\text{—B—B}\ldots$$

$$\ldots\text{B—B—}\dot{\text{B}}\text{—B—B}\ldots + \text{A} \rightarrow \ldots\text{B—B—B—B—B}\ldots$$
$$\qquad\qquad\qquad

acetate in benzene solution. For this system the rate of reaction is reduced manyfold by the addition of small quantities (e.g., one per cent) of benzene.

One might expect that the simplicity of the technique would have led to a much wider application, but it appears that the disadvantage of relatively elaborate separation procedures have placed a severe limitation on its use. Attempts have been made to produce modifications of natural high polymers, notably rubber, by grafting vinyl polymers on to the polyisoprene trunk. It is well established that monomers, such as vinyl acetate and methyl methacrylate, polymerize quite freely in the presence of the diisoprene, dihydromyrcene, with a reduction of molecular weight corresponding to the efficiency of the additive as a transfer agent. It would appear likely therefore that the corresponding polymerizations in the presence of natural rubber would give rise to branched products according to the scheme outlined above.

The system was carefully examined by Merrett (12a, 12b) who polymerized methyl methacrylate and styrene in the presence of rubber using benzoyl peroxide or using 2,2-azoisobutyronitrile as an initiator. The presence of about five per cent by volume of rubber using the benzoyl peroxide initiator was calculated to give the molecular weight of polymethyl methacrylate as 432,000 instead of 750,000 in the absence of rubber. The average molecular weight of the free polymer and of the branches ought to be identical, but it was found that not only were the branches much smaller than was anticipated but also the ratio of bound to free polymethacrylate was much in excess of that expected, about 1.2 instead of 0.76. Repetition of the experiments, replacing methacrylate with styrene, showed both these effects to be much enhanced. These results show that the number of points of attachment on the rubber chain exceeds that required on a simple transfer mechanism by a factor of about 100. This figure is obviously based on the supposition that intramolecular transfer is excluded. Even if this possibility is entertained, the fact that almost 50 per cent more vinyl polymer than predicted is incorporated in the rubber seems incapable of explanation.

When 2,2-azoisobutyronitrile was used in place of benzoyl peroxide, the picture altered completely and very little graft polymer was produced This suggests that almost all grafting in the benzoyl peroxide-initiated reaction follows from an attack upon the rubber molecule of the radicals generated from benzoyl peroxide. The well-known fact that isobutyronitrile radicals show no tendency to abstract hydrogen even at relatively high temperatures (13) ensures that no interaction between these radicals and rubber molecules occurs.

An extension of this study has recently been carried out using styrene as monomer and 2,2-azoisobutyronitrile, bis-1-hydroxycyclohexyl peroxide, and benzoyl peroxide as initiators (14). In support of the previous results it is found that the grafting efficiency is lowest with 2,2-azoisobutyronitrile and highest with benzoyl peroxide. In all cases the grafting efficiency decreases as the concentration of initiator increases. This latter fact appears

to be at variance with the mechanism suggested by Merrett for the benzoyl peroxide-initiated reactions. The over-all rates of polymerization $R_p$, are given by the empirical equation:

$$R_p = \frac{K}{1 + A[\mathrm{R}]}[\mathrm{M}]^{\alpha}[\mathrm{I}]^{\beta}$$

where [R], [M], and [I] are the concentrations of rubber, monomer, and initiator, respectively, and $K$, $A$, $\alpha$, and $\beta$ are constants. For 2,2-azoisobutyronitrile as the initiator, $\alpha = 1.2 \pm 0.02$ and $\beta = 0.5 \pm 0.01$. Thus in most features the usual kinetics are obeyed, although there is a definite retardation of the reaction due to the rubber.

The difficulty which was encountered in the separation of the desired graft product from either homopolymer is apparently avoided if the preformed polymer is present as microgel (15). This method is not general in that at least part of the molecule is relatively highly cross linked. In these experiments (16) microgel was formed by copolymerization of the pairs, methyl acrylate and divinyl benzene, acrylonitrile and methylene bisacrylamide. The microgel was dispersed in water with either styrene or acrylonitrile monomer. Ultracentrifuge investigation of the product after polymerization of the added monomer showed that the quantity of homopolymer was very small compared with the grafted material. Separation of 100 per cent grafted polymer was effected and this was shown to be free of entangled homopolymer.

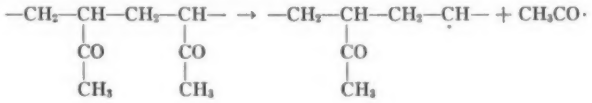
Microgel can be dispersed in the usual polymer solvents to give thermodynamic true solutions (17), and it is demonstrated that the intrinsic viscosity of the original microgel and the grafted polymer substantially obeyed Einstein's law for solid spheres.

One of the interesting features of this process is that the microgel retains a considerable free radical activity over a long period of time (100 days or more). Consequently if all the polymerization of the second monomer is initiated by these "frozen in" radicals, the product will undoubtedly be 100 per cent grafted material. Homopolymer can appear only if other substantial types of initiation, e.g., thermal, take place, or if there is any appreciable tendency towards transfer to monomer. Because the polymerization reaction occurs only in or very near the microgel particles, it may be that there is an overwhelming advantage to the polymeric particles in competition with monomer for transfer reaction. This must imply that considerable intramolecular transfer occurs.

*Creation of active centers on suitable polymer.*—A modification of the method described in the previous section involves the creation of suitable centers of reaction on the main chain of a preformed polymer in the presence of a second monomer. These new centers may be free radicals which are capable of initiating the polymerization of this monomer that will add as branches to the main trunk. A second possibility is that the active centers

so created may be capable of undergoing a condensation reaction with the ends of a second polymeric molecule. Both methods have been used although the former is the more popular.

Photolysis of poly ketones in which the ketonic groups appear as side chains will give rise to free radicals on the main chain. Initiation by such macroradicals has been found to give branched molecules (17). Using polymethylvinylketone irradiated in dioxan solution with ultraviolet light of 3130 A., two reactions are possible



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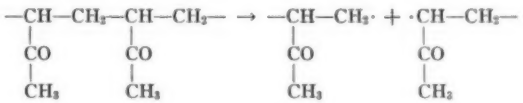


In the first of these processes, the acetyl (or methyl) radical is hydrogenated by reaction with a solvent to give acetaldehyde (or methane). The second process brings about degradation of the polymer. Consequently, in the presence of another monomer both block and graft polymers are formed, although the latter is likely to predominate.

Melville & co-workers (18) were able to partially photobrominate polystyrene so that the added bromine atoms were on the $\alpha$ carbon atoms. Photolysis of this polymer gives radicals on the main chain on which branches can be formed. This method has the disadvantage that the released bromine atoms also induce polymerization of the added monomer so that the final material always contains homopolymer.

A reasonable alternative to bromination of polystyrene should be oxidation to hydroperoxide—these groups being in the $\alpha$ position. Such a reaction appears to be sterically impossible. Musrobian (19, 20, 21) used *p*-isopropyl styrene as the polymer. Oxidation of this polymer occurs at a rate comparable with that for the oxidation of cumene. The resulting product will have hydroperoxy groups arranged along the chain. When this polymer dissolved in a second monomer and emulsified in water, the hydroperoxy groups are decomposed in presence of ferrous ion. This gives free radicals on the polymer but using such a redox system radicals are produced singly as a result of electron transfer, thus

$$ROOH + Fe^{II} \rightarrow OH^- + Fe^{III} + RO\cdot$$

In this way the production of a second polymer is avoided and the separation problem is substantially eliminated.

The production of hydroperoxides on a suitable polymer can be brought

about under γ-irradiation in the presence of air or oxygen. This method was first used by Chapiro (22 to 25). Polyethylene, when treated in this way, can be used to initiate the polymerization of monomers such as acrylonitrile, methyl methacrylate, and vinyl carbazole. The most interesting feature of this reaction is the quite abrupt diminution in activation energy for the polymerization process when the temperature exceeds 100°C. Thus for methyl methacrylate polymerization the activation energy above 97°C. is 8.6 kcal. per mole, while below 97°C. the value increases to 16.2 kcal per mole. This is interpreted as being due to the fact that above about 100°C. the crystallites are completely melted and so free diffusion of the monomer through the polymer is possible. Below 100°C. free diffusion is impaired.

A similar study using polyethylene may necessitate a variation of the latter interpretation (26). The number of hydroperoxy groups introduced by irradiation can be estimated by heating at 77°C. for 15 hr. in the presence of 1,1-diphenyl-2-picryl hydrazyl. The uptake of this radical scavenger can be estimated easily by optical density measurements. After this treatment, further heating in boiling xylene resulted in the uptake of more scavenger. This is taken to mean that peroxides, as well as the hydroperoxide groups, also occur which are somewhat more stable. This obviously would complicate any kinetic investigation over the range of temperature examined by Chapiro (25).

It is not necessary to bring about hydroperoxide formation in order to form graft copolymers. Modification of rubber by grafting of vinyl polymers on the trunk polyisoprene has been accomplished by direct irradiation of a rubber latex to which methyl methacrylate has been added (27, 28). The material resulting from such treatment contains little (if any) homopolymer, which must be taken to imply that all initiation occurs from radicals formed on the rubber. Homopolymer is naturally formed when very efficient transfer agents, e.g., mercaptans, are used to limit the lengths of the side chains. Similar experiments have been carried out by Sebban-Danon (29) who studied the effect of γ-radiation on solutions of polyisobutylene in styrene. Polymerization of styrene is initiated as a result of radical formation both from the polymer and styrene. The former predominates in view of the considerably higher G value, 6 to 7 (30), compared with 0.46 for styrene (31). The reaction exhibits a very pronounced gel effect. The rate is proportional to the square root of the irradiation intensity in the early stages, but at relatively high conversions the exponent is demonstrably greater than 0.5.

This type of investigation has been further studied by Henglein & others (32, 33) who have examined the systems polymethyl methacrylate-acrylonitrile, polymethyl methacrylate-vinyl pyrrolidone, and polyisobutylene-styrene. The results are very much in accord with those just discussed, although they also include the demonstration of a diffusion effect. Other acrylic polymers have been subjected to radiation grafting in like manner but details are not readily accessible (34). Grafting of vinyl polymers on nylon has been reported by Bevington & Eaves (35).

The high energies of γ-radiation are not altogether necessary to promote

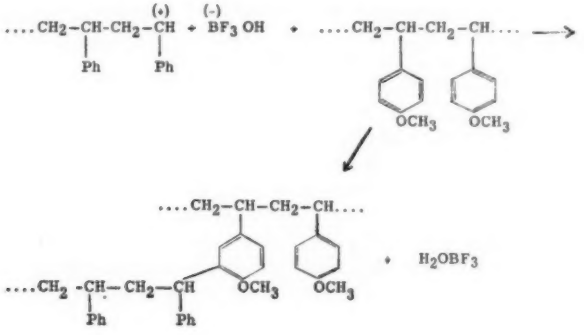
grafting reactions. With suitable sensitizers such as benzophenone or 1-chloroanthroquinone ultraviolet light has been shown to bring about grafting of styrene, methyl methacrylate (36), and acrylamide (37) on natural rubber. The reaction is usually carried out in emulsion, i.e., natural rubber latex to which monomer and sensitizer are added. Although the efficiency of the photochemical process is low since much of the light is reflected, it is possible to achieve 90 per cent conversion of the added monomer of which only two per cent appears as homopolymer.

In some of the foregoing methods it has been shown that the amount of adventitious homopolymer can be kept very low, but a recent technique makes almost certain that the sole product will be the graft polymer. The technique depends on an extension of the reaction of ceric salts with alcohols. The complex initially formed decomposes to give a free radical probably on the $\alpha$ carbon atom—this being the only radical formed (38, 39).

$$Ce^{IV} + RCH_2OH \rightleftharpoons \text{complex} \rightarrow \underset{(\text{or } RCH_2O\cdot)}{\dot{R}CHOH} + Ce^{III} + H^+$$

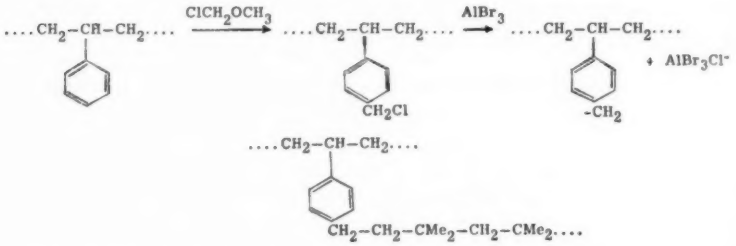
It is evident that if this reaction is applied to polyvinyl alcohol graft copolymers will be formed. Grafts of acrylonitrile and acrylamide on polyvinyl alcohol have been successfully prepared and demonstrate the efficacy of the technique (40). It is reported that several natural polymers such as cellulose, dextrans, starches, and polygalactosides have been used as backbones. Synthetic polymers formed in the presence of small amounts of acrolein have also proved useful. All reactions are carried out in emulsion.

*Ionic mechanisms.*—It is well known that certain polymers can be formed by an ionic rather than radical mechanism, so that it would appear plausible that creation of a carbonium ion on a polymer chain might lead to graft reactions under suitable circumstances. The amount of work available in this field is small but requires brief comment. Haas & his collaborators (41, 42) have studied ionic chain transfer as a method of grafting, using the same sort of principle as described in the discussion on radical attack, above. The reaction scheme for styrene on poly-*p*-methoxystyrene can be written as



Substitution on the aromatic nucleus in the manner described is rather surprisingly limited to the addition of polystyrene chains. Thus it has not been found possible to carry out the following grafting reactions: alkyl vinyl ethers, isobutylene, N-vinylpyrrolidone on polystyrene, polyvinyltoluene, or poly-*p*-methoxystyrene. The reason for this intransigence is but slightly understood.

It is possible however by suitable modification of polystyrene to bring about grafting through the aromatic portions of the molecule. Smets & Kockelberg (43) have chloromethylated polystyrene and have shown that, in the presence of aluminium bromide in carbon disulfide solution, isobutylene may be grafted on to the polystyrene trunk chain. The whole scheme is




The main difficulty in these experiments lies in the choice of a suitable solvent and in the partial insolubility of the polymer after addition of the aluminium halide.

Plesch (44, 45) has recently described an ionic method akin to the creation of radical centers on the body of a preformed polymer chain. If polyvinyl chloride is treated with aluminium halides or titanium tetrachloride one might reasonably expect a reaction such as

$$....CH_2—CHCl—CH_2—CHCl.... + AlCl_3 \rightarrow$$

$$....CH_2—\overset{+}{C}H—CH_2—CHCl.... + AlCl_4^-$$

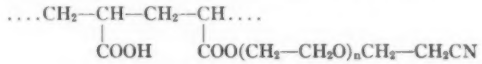
The macrocarbonium ion ought to be capable of initiating polymerization of a suitable monomer such as styrene. This has been demonstrated to be the case both by Plesch and by Teyssie & Smets (46).

Both polyvinyl chloride and vinylidene chloride-vinyl chloride copolymers have been used as stem polymers and grafts with styrene, indane, indole, and *trans* stilbene. Degradation and discolouration of the product is avoided by working at low temperatures and using titanium tetrachloride in preference to aluminium halides.

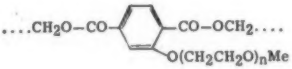
*Condensation methods.*—All the techniques which have been described imply that the length of the branches is governed by a distribution function, and it is not possible to regulate either the length or the number of branches per stem molecule. It would be desirable for many purposes to be able to

attach branches of known length and known number to the stem. This is possible by making use of condensation procedures, whereby fractionated polymers possessing suitable end groups are condensed with fractionated polymer containing a known number of complementary functional groups per chain and which are distributed along the chain.

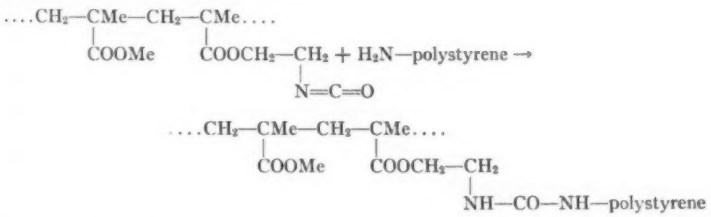
Using such condensation methods it is possible to attach polyethylene oxide or polyethylene imine to polyhexamethylene adipamide (nylon) and cellulose (47, 48). Equally branches of polyethylene oxide have been attached to polyacrylic acid (49) giving structures such as



or to polyethylene glycol terephthalate (dacron) in which the polyoxide substitutes on the aromatic nucleus (50), thus



An interesting and potentially versatile method belonging to this general class has recently been elaborated by Graham (51). When polystyrene is prepared by an anionic mechanism using sodamide as initiator the polymer contains terminal amino groups. These groups readily condense with isocyanate groups on a copolymer prepared from a feed containing a small quantity of $\beta$-isocyanoethylmethacrylate. A typical copolymer of methyl methacrylate and the isocyanate substituted monomer in the ratio 55:1 gave the required graft product:



It is evident that this procedure can give very precisely defined graft copolymers, since the number of isocyanate groups can be readily evaluated. Thus for a closely fractionated sample of the copolymer the number of branching sites per molecule is known. Also it is possible to fractionate the polystyrene, and so branches of a predetermined length may be introduced onto the backbone.

A similar approach has been employed by Melville, Peaker & Vale (52). Linear polyvinyl acetate prepared at $-20°C.$ was hydrolysed to give the corresponding polyvinyl alcohol. Complete hydrolysis at this stage ensures

that no adventitious branch formation survives. The product was reacetylated using acid labelled with $C^{14}$, and fractionated. Partial hydrolysis of a fraction gave a copolymer of vinyl alcohol and vinyl acetate for which the hydroxyl content was readily assessed from the change in radioactivity. In order to introduce branches it is most convenient to prepare a second polymer possessing carboxyl end groups. A convenient initiator for this purpose is 4,4′azo-4-cyano-pentanoic acid (53). Since the vinyl acetate termination reaction is predominantly by disproportionation (54), and there is also a large transfer constant to monomer (55), it is unlikely that any molecule will possess two carboxyl groups. Condensation of a fraction of this polymer was effected by first coverting the carboxyl-ended material to the acid chloride with thionyl chloride, or by a straight esterification reaction in tetrahydrofuran solution using trifluorocetic anhydride as catalyst. Table I shows the composition of the polymers.

TABLE I

COMPOSITION OF BRANCHED POLYMERS OF VINYL ACETATE

| No. av. mol. wt. of branches | Viscosity av. mol. wt. of backbone | Av. no. of branches per molecule | No. of branches per 1000 monomer units | Huggins constant k′ |
|---|---|---|---|---|
| 14,500 | 1,045,000 | 19 | 1.60 | 0.46 |
| 14,500 | 827,000 | 23 | 2.41 | 0.57 |
| 16,000 | 508,000 | 15 | 2.47 | 0.59 |
| 16,000 | 508,000 | 13 | 2.14 | 0.53 |
| 16,000 | 651,000 | 35 | 4.68 | 0.63 |
| 16,000 | 651,000 | 40 | 5.34 | — |
| 8,000 | 651,000 | 13 | 1.70 | 0.43 |

The Huggins constant, k′, is evaluated from the slope of the reduced viscosity concentration plot. The value for the initial partially or fully acetylated polymers lies between 0.33 and 0.38, and it will be seen that this value is much exceeded by the branched material and, further, k′ increases markedly with the extent of branching.

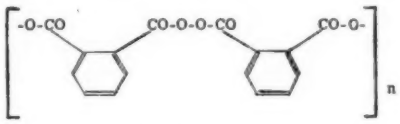
### SYNTHESIS OF BLOCK COPOLYMERS

The preparation of block copolymers poses a somewhat more difficult problem than that of graft copolymers. In the latter there is a multiplicity of possible sites of reaction while to form block copolymers a limitation is imposed insofar as addition takes place end to end. The tedious procedure of purification is approximately the same in both cases.

*Use of polymers with labile end groups.*—Adaptation of a grafting procedure can be devised so that a free radical created at the end of a macromolecule is used to initiate polymerization of a second monomer. This can be

accomplished by ensuring that the preformed polymer possesses end groups which by photolysis will yield a macro radical. Polymerization of most vinyl monomers in the presence of carbon tetrabromide or trichlorobromomethane ensures that almost all the polymeric molecules possess a tribromomethyl or trichloromethyl end group. The polymer may then be isolated and dissolved in a second monomer and irradiated with light of requisite energy to cause scission of the carbon-halogen bond releasing a halogen atom and giving a free electron on the end of the polymer molecule. This method was successfully applied by Melville, Dunn & Stead (55) to the preparation of block copolymers of styrene and methyl methacrylate. As with many of these reactions, the homopolymer, consisting of unchanged initial polymer and that arising from other modes of initiation in the second stage, makes separation of the block copolymer a difficult operation.

By using a polyperoxide, preferably diperoxide, to initiate polymerization, it is possible to isolate a polymer having peroxide links either in the end groups or in the macromolecule itself. When a solution of this polymer in another monomer is heated, scission of the peroxy groups brings about polymerization of the second monomer. This is fairly readily accomplished since the first polymerization can be stopped when approximately half the peroxide groups have been consumed, thereby assuring that an adequate number are present on the ends of, or in, the chain of the polymer. This method was adopted by Smets & co-workers (56, 57, 58) to investigate several possible pairs of monomers using polymeric phthalyl peroxide.




Polystyrene prepared by using phthalyl peroxide was able to initiate polymerization of methyl methacrylate but not vinyl acetate nor vinyl pyrrolidone; polyvinyl acetate prepared in the same way initiated polymerization of styrene.

A variation of this method has been described, making use of the dihydroperoxide of *m*-di-isopropyl benzene (59, 60). In the original work, a thermal polymerization of one monomer was carried out using the dihydroperoxide as initiator. When about half the hydroperoxy groups was consumed the polymer was isolated and dispersed in aqueous medium with a second monomer, along with ferrous ion, giving a convenient redox initiating system with the hydroperoxide. Only one radical is produced in this way and consequently the formation of homopolymer is largely avoided. Urwin (61) has further elaborated the technique by carrying out the first stage of the reaction in the presence of cumenyl mercaptan as a transfer agent. This ensures that all the polymer molecules formed have either a terminal hydroperoxy or a *p*-isopropylphenyl group. The latter is readily oxidised to a hydroperoxide

and thus the second stage becomes more efficient. By careful experimental procedure this more elaborate method should give rise to almost pure block copolymer with little need for separation.

A possible variation of the grafting transfer technique has been studied by Bamford & White (62). When polymerization of a vinyl monomer is carried out in the presence of a tertiary amine, using fairly high amine: monomer ratios, almost all the polymer molecules, which are isolated, possess a tertiary amine end group. The polymer is dissolved in a second monomer which undergoes polymerization and furthermore transfers preferentially with the end groups of the dissolved preformed polymer. This gives the required end group radical on which block copolymers can be formed. Bamford & White demonstrate the production of block copolymers of methyl methacrylate and acrylonitrile by this process. The mechanism appears to be:

$$A_n + RCH_2 \cdot NR'R'' \rightarrow A_nH + \dot{R}CH \cdot NR'R''$$

$$\dot{R}CH \cdot NR'R'' + A \rightarrow R{-}\underset{\displaystyle NR'R''}{\underset{|}{CH}}{-}A \cdot$$

Transfer in the second monomer is supposed to involve the second methylene hydrogen of the group already taking part in the reaction, so that

$$B_m \cdot + R{-}\underset{\displaystyle NR'R''}{\underset{|}{CH}}{-}A_n \rightarrow B_mH + R{-}\underset{\displaystyle NR'R''}{\underset{|}{\dot{C}}}{-}A_n$$

$$R{-}\underset{\displaystyle NR'R''}{\underset{|}{\dot{C}}}{-}A_n + B \rightarrow A_n{-}\underset{\displaystyle NR'R''}{\overset{\displaystyle R}{\underset{|}{\overset{|}{C}}}}{-}B \cdot$$

so that a block copolymer is built up with the two polymer sequences joined by RCNR′R″.

Radicals whose lifetime is relatively long could, in principle, always be used for creating block copolymers. Thus it might be argued that the method used by Shashoua & van Holde (16) is more likely to produce block copolymers since the simplicity of the technique arises from the fact that microgel is capable of retaining free radicals over long periods of time. These radicals have been shown to be capable of initiating polymerization of other monomers. It would be unlikely that such "frozen in" radicals are congregated on the main chain, and indeed they are more likely to be either at the end of the main chain or at the end of branches already present. This underlines one of the major difficulties in assessing the validity of the methods which have been described. In very few cases has a definite attempt been made to characterise the final polymer with certainty; the structure is usually de-

duced by reference to the likely course of the reaction provided some assumption is fulfilled.

Melville & co-workers (64a, 64b) devised a method whereby a monomer was allowed to stream through a capillary into a second monomer. On its passage down the capillary the monomer was subjected to intense ultraviolet radiation so that a very high concentration of radicals was achieved. By suitably arranging the rate of flow and the distance from the point of illumination to the exit, it is possible to ensure that most of the radicals formed in the illuminated zone survive to enter the second monomer. The issuing stream is rapidly dispersed in the new monomer which polymerizes on the former radicals. It has been demonstrated, using butyl acrylate as the streaming monomer, that block copolymers are possible products. Funt & Collins (63) have used a similar technique to prepare block copolymers of butyl acrylate with styrene and vinyl pyridine. They find the calculated yield of polymer agrees reasonably well with experiment. It might be argued with some justification that the section of the molecule added after the radical enters the second monomer will be a random copolymer of the two monomers but will incorporate probably only a small amount of the first monomer. This arises since the unchanged first monomer will also be discharged into the second monomer. A further point with regard to this method is that the first block will, under normal circumstances, be considerably smaller than the second. Yields of block copolymer are very small.

Emulsion methods have been advocated for the formation of block copolymers. The systems, which can be used in the method originally suggested by Melville & Dunn (64a), are limited by the fact that one monomer must be soluble in the extended phase, usually water, while the other has to be insoluble but is emulsified in the solution by using a suitable soap. The initiator is soluble in the extended phase and therefore brings about the polymerization of the soluble monomer. Eventually this radical penetrates a micelle containing the insoluble monomer which adds to the entering radical. While, in theory, this method appears infallible, the differentiation in solubility is not so sharp as has been suggested. It is likely therefore that the blocks will themselves be copolymers of a vastly differing composition. Dunn and Melville concentrated on the systems styrene-acrylic acid and styrene-methacrylic acid. It has been reported that block copolymers of vinyl acetate and methacrylic acid also yield block copolymers in emulsion. These were examined after alkaline hydrolysis and showed only a very slight tendency to form lactones, thereby demonstrating their difference from the random copolymers of the same composition (65).

A second method in which emulsions can be used is as follows (59). Irradiation of a water emulsion of a suitable monomer such as styrene with high energy radiation for a short period of time (usually 10 to 15 min.) starts the reaction which then will continue at a nearly steady rate until most of the monomer is used up. At this stage a second monomer similarly emulsified, is added and the polymerization continues by virtue of the radicals trapped

in the polymer (latex) particles. It is undoubtedly true that the amount of block copolymer relative to the homopolymer is low, using such a technique. The use of radiation is of interest in that it avoids the creation of further centers in the second stage of the process.

*Scission of macromolecules.*—Scission of a polymer molecule must produce two fragments, each of which is a free radical. The most convenient method of breaking polymer chains is by a mechanical degradation process. This can be carried out by ultrasonic irradiation, high speed stirring of solutions of polymer, or by milling swollen polymer. All of these processes create high shear forces in the polymer, which are sufficient to bring about scission. The earliest work on ultrasonic irradiation proved to be unsuccessful (66), but since then many such applications have been proved (67, 68, 69). The usual technique is to irradiate a solution of a polymer in a second monomer. The formation of free radicals in the scission process initiates polymerization of the second monomer. An attractive procedure would be to irradiate a solution of a mixture of two polymers in an inactive solvent. Provided that all the free radical fragments combine and do not disproportionate, it is likely that unlike radicals will combine to give block copolymers.

With all the mechanical methods it is apparent that their nonselective nature means that the block polymer after formation is also liable to undergo scission so that it is possible to produce copolymers with multiple blocks, although this feature of the method does not appear to have been seriously considered. If this phenomenon occurs then there must be an optimum time of irradiation beyond which random copolymer would appear.

Milling polymer, which is softened at elevated temperature or by imbibing suitable liquid, causes scission. The method has been used more particularly in preparing block copolymers involving rubber (70 to 74). The usual method adopted is to swell the rubber with a suitable monomer when polymerization occurs in the manner already outlined. It is also possible to mill a mixture of rubber and another polymer when the simultaneous scission of the two polymer molecules and subsequent combination of the unlike free radicals gives the required block polymers. An interesting extension made by Kargin & co-workers (75) has produced block copolymers by milling phenol formaldehyde and nitrile rubber. It is claimed that the polymers so obtained have increased strength but much decreased elasticity; they are soluble in both acetone and benzene. Watson (76) has indicated that the method is capable of extension to many combinations of polymers (77).

*Living polymers.*—This is a somewhat specialised method which can be applied to conjugated hydrocarbons such as styrene, butadiene, isoprene, and methyl methacrylate. All of these monomers can be polymerized in the presence of ionic "salts" of aromatic hydrocarbons such as $Na^+$ naphthalene$^-$. With the hydrocarbons the resulting polymer is still active and other suitable monomers are polymerized on addition to the system. Thus styrene can be polymerized completely, followed by methyl methacrylate. The

latter gives a self-terminating system so that no further polymerization is possible (77 to 80).

*Chemical Methods.*—As with graft copolymers, none of the methods already described gives a means of controlling either the size or the frequency of blocks. Using the dihydroperoxide technique, it is possible to fractionate the first polymer after preparation so that the length of at least one block is fixed. Fractionation of the total block will presumably give products of both constant composition and molecular weight.

It is possible to envisage methods whereby polymers may be prepared with suitable end groups which may be condensed either *inter se* or by the use of a suitable bifunctional molecule. The methods of preparation of molecules with the right kinds of end groups are well established, so that molecules with one or two hydroxyl or carboxyl ends would be easily obtained. Condensation of these to effect their union through an ester group (probably after conversion of the carboxyl to an acid chloride) appears to be a feasible proposition, at least, in theory. However, it is doubtful if, even in the presence of a catalyst, the concentration of functional groups which could be attained would be great enough to give a reasonable reaction rate. Indeed, emphasis has been placed on the use of polymers with identical ends, usually hydroxyl or carboxyl, and effecting linkage with dibasic acids, diisocyanates, or dihydric alcohols. By using large excesses of the latter a reasonably rapid reaction takes place (81, 82). The second method is nonselective so that molecules of either homopolymer could interact without block formation. Consequently a separation difficulty still exists. In the first method only unlike molecules would interact so that at high conversion very little of either homopolymer would remain.

One of the biggest gaps in the field appears to be the lack of information on block copolymers involving vinyl and condensation polymers. As has been indicated earlier there is some evidence that such polymers have been made by the milling process (75), but otherwise little or nothing appears to be known. At the same time, it is obvious that either of the chemical techniques described above could be made to yield blocks with, say, polyesters and polyamides.

The problem of preparing block copolymers of condensation polymers is almost trivial since it is evident that the nature of the condensation reaction allows easy extension to this field. Furthermore one might expect to obtain alternating blocks under suitably controlled conditions (83).

## Purification of Polymers

The eventual assessment and characterization of graft and block copolymers lies in the study of their solution properties compared with the properties of random copolymers of like composition. Before such a task can be undertaken it is necessary to achieve purification of the nonrandom copolymer and also some measure of fractionation The purification proce-

dures which have been described all depend on modifications of methods which have been employed to purify homopolymers, i.e., a process of separating very large from small molecules. No known systematic study of the problem of separating large molecules of one chemical type from large molecules of another type has been undertaken. At best, as a result of most of the methods described, it is necessary to separate the required copolymer from a homopolymer.

If precipitation methods are used, two possible variations in solubility with solvent composition are possible. The first is the well known variation due to molecular weight; the second, which may be the more serious, is variation due to composition. In practice it is likely that these effects give an overlap so that a relatively small molecule of the copolymer has the same solubility as a larger molecule of the homopolymer. At worst, such an overlap in solubility properties would limit the useful yield of a preparation. In producing a fraction of the copolymer itself, by which it would be hoped to obtain a resonably sharp molecular weight distribution within the fraction, the same sort of overlapping could make nonsense of the whole procedure.

If it has been arranged that the parts of the copolymer have very different solubilities, it may be that this difficulty will in part disappear since one homopolymer will be very much more soluble than the other, and presumably the solubility of the copolymer will be intermediate. At the same time, many of the copolymers would not conform to this sort of behaviour.

## Studies of Solution Properties

Systematic studies of the solution properties, i.e., viscosity, osmometry, and light scattering, of nonrandom copolymers have been limited to graft copolymers. In view of the remarks of the previous section it is a difficult problem to decide to what extent one can apply a quantitative interpretation to the data recorded. Merrett (12) examined the osmotic behaviour of graft copolymers of polystyrene on rubber. While it has been generally assumed that the presence of branches would give rise to a change in the slope of the reduced osmotic pressure-concentration curve (84, 85, 86), in this instance the value obtained for the grafts is about the same as for material rubber. This is in line with results from the swelling of lightly crosslinked rubbers (87).

A study of branched polystyrene, prepared by the redox-initiated polymerization in the presence of oxidized polystyrene or copolymers of styrene and 4-vinyl cyclohexene-1, has recently been reported (88). In this paper, attention is focussed on the solution viscosity relationships, since it is known that the intrinsic viscosity of a branched molecule is less than that of a linear molecule of the same molecular weight (89, 90). A second, and probably less effective method, is the determination of the Huggins' constant, $k'$, from the slope of the reduced viscosity-concentration curve. Empirically, a relationship has been found between the presence of branching and unusually high values of $k'$ (91, 92, 93).

Despite the fact that there is incontrovertible evidence that grafted branches are created, it is found that the k′ values in butanone solution lie between 0.39 and 0.41, as is also found for the presumably linear starting material. Manson and Cragg suggest that k′ is not measurably affected by the presence of a relatively small number of linear branches but may well be sensitive to the presence of branched (bushy) branches. This is probably reasonable in that k′ is a function of the segment density in the molecular coil (94), and for a lightly branched molecule this would obviously be little different from the linear molecule. An increase in k′ is suggested as a method of demonstrating the existence of bushy branches.

It will be seen that the k′ factor as measured by Melville, Peaker & Vale (52), increases as branching becomes heavier (Table I). This is in contradiction to the results of Manson & Cragg (88) and may imply that in polyvinyl acetate there are bushy branches which, indeed, is not improbable despite the precautions taken to eliminate these branches.

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# ION EXCHANGE[1]

By Harold F. Walton[2]

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At a conservative guess, over five hundred publications directly relating to ion exchange appeared in 1958. Many of these deal with specific technical applications and are inappropriate for a review such as this. Some, however, describe developments which are radically new. The new class of inorganic exchangers based on hydrous oxides of the fourth, fifth, and sixth group of the periodic table is such a development. Advances have also been made in the thermodynamic interpretation of ion exchange, in the mathematical treatment of diffusion into ion exchangers and of ion exchange membrane phenomena, and in understanding the physicochemical nature of ion exchanging materials.

One new book on the subject has appeared, the second edition of Kunin's *Ion Exchange Resins* (1). It is larger than the first edition and includes new material on hydrometallurgy, resin synthesis, membranes, and liquid ion exchangers. It is primarily a reference work for those who use ion exchange in the chemical industry. For the laboratory worker who uses ion exchange as a research tool, a good review is the article by Griessbach (2) in the new edition of Houben-Weyl's *Methoden der organischen Chemie*. The same treatise carries an article by Manecke (3) on redox resins.

New developments in ion exchange and the present state of its theory are reviewed comprehensively by Helfferich (4). An excellent, short user's guide to ion exchange resins was published by a leading chemical supply house (5). Reviews by Kunin & collaborators, one on ion exchange as a unit process, the other on its analytical applications, have been appearing annually for some years and continue to be extremely useful (6 a, b). In Scandinavia, Sjöström has published a short review (7).

A symposium on ion exchange in the chemical industry was held in Leipzig in 1958 (8). An extensive symposium was held in Leningrad in 1957, and is now available in an English translation (9); it has special reference to the food and pharmaceutical industries, but includes papers of fundamental theoretical interest. A symposium on diffusion into gels was held in Paris in 1957; the papers have now been published in the *Journal de chimie physique*, and several relate to ion exchanging materials. The Second United Nations Conference on the Peaceful Uses of Atomic Energy, held in September, 1958, included several important papers on ion exchange. Abstracts of some of these have already appeared (10). A new journal of interest to those who use ion exchange began publication in 1958 (11).

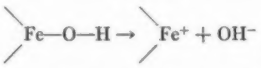
[1] The survey of literature was completed December 15, 1958.

[2] The reviewer is deeply indebted to Dr. C. Calmon of the Permutit Company for permission to use the comprehensive bibliography which he has compiled.

## Inorganic Ion Exchangers

*Synthetic materials.*—A very interesting development of the past year has been the production of ion exchangers based upon hydrous metal oxides. These materials are stable to heat and radiation, which makes them very attractive for the atomic energy field. Two research groups have made major contributions to this development, one at Harwell under Amphlett (12, 13, 14), the other at Oak Ridge under Kraus (15).

It has been known for many years that precipitated hydrous oxides, such as $Fe_2O_3$, have ion-exchanging properties. Their colloidal particles carry an electric charge which can be attributed to surface ionization. Thus, hydrous ferric oxide probably carries surface hydroxyl groups which ionize as follows:

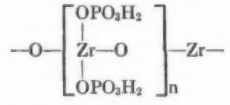


Below pH 9, precipitated ferric oxide carries a positive charge and adsorbs anions strongly. These anions can be exchanged for others in solution. At higher pH the charge is reversed and the material absorbs cations instead.

Many hydrous oxides, including $Al_2O_3$, $Cr_2O_3$, $Bi_2O_3$, $TiO_2$, $ZrO_2$, $ThO_2$, $SnO_2$, $Nb_2O_5$, $Ta_2O_5$, $MoO_3$, and $WO_3$, adsorb and exchange cations and anions from solution. Their isoelectric points vary widely and are influenced by the method of preparation, but all may be considered as amphoteric ion exchangers. Generally, the more basic the oxide, the higher the isoelectric pH; thus $ThO_2$ is isoelectric at pH 9.8, $SnO_2$ at pH 4.8. At the isoelectric point the materials adsorb both cations and anions, suggesting a heterogeneity of exchange sites.

A limitation to the use of these oxides as ion exchangers is their solubility in acid or alkaline solutions. The oxides of Group IV elements are the least soluble. Hydrous zirconium oxide, $ZrO_2$, dissolves in strong acids but is essentially insoluble above pH 2. Up to pH 6 or 7, zirconium oxide acts as an anion exchanger; at higher pH values it becomes predominantly a cation exchanger.

By combining Group IV oxides with the more acidic oxides of Groups V and VI, materials are obtained which are primarily cation exchangers and are extremely insoluble. By mixing solutions of zirconyl chloride and phosphoric acid, for example, solid products with variable $ZrO_2$: $P_2O_5$ ratios are obtained, which can be regarded as phosphoric acid rendered insoluble by crosslinking with zirconium oxide. A possible formulation is



Such a compound would have an equivalent weight, as an acid, of 75, or a cation exchange capacity of over 13 m.eq./g on a dry basis. Products with capacities approaching this have, in fact, been obtained. This is much higher

than the exchange capacity of ion exchange resins, especially when compared on a volume basis. The materials are weak acids, however. They show at least two stages of neutralization, as would be expected; maximum ionization is reached at pH 12. Similar materials can be produced using arsenic, molybdic, and tungstic acids in place of phosphoric acid, and titanium and thorium in place of zirconium.

To be suitable for ion exchange use, these materials must be prepared in proper physical form. Conditions of precipitation and drying are important. The Oak Ridge group has prepared granular precipitates which have high exchange capacities and react rapidly with solutions. They are, however, unsuited for large-scale column operation because of their small particle size. The Harwell group, on the other hand, has concentrated on preparing gels which dry to give coarse particles like the familiar synthetic aluminosilicate exchangers. These are very permeable and will accommodate large ions, such as ferrous tris-orthophenanthroline. They can be used in column operation at high flow rates. They are, however, difficult to prepare in a reproducible manner. These differences between the gels and the precipitates must be kept in mind when comparing data of the two research groups.

Several interesting separations have been made with these exchangers. Rubidium and cesium are clearly separated on columns of zirconium phosphate or tungstate [Crouch *et al.* (16)], and a column of zirconium molybdate separates strontium and barium very well (14). The alkali metals can be separated as a group from the alkaline earths, and these, in turn, from yttrium and the rare earths. The elution bands are sharp and symmetrical, and recoveries are quantitative. Operation is fast enough that short-lived isotopes can be separated (16). Because the exchangers are derived from weak acids, the pH of absorption and elution is very important.

Other researchers have been active in preparing new artificial inorganic exchangers. Silicate and phosphate gels are effective in removing trace amounts of fluoride ions from solutions [Taylor & Jensen (17)]. The anion-exchanging properties of a number of precipitated metal oxides were studied by Hayek & Schimann (18). Salts of heteropoly acids, such as ammonium phosphomolybdate, can be used in columns to separate the alkali metals [Smit (19)].

The first artificial ion exchangers ever made were aluminosilicates, and yet the possibilities of this class of exchangers are by no means exhausted. A new technique for preparing aluminosilicate gels was described by Aleskovskii & Golovanov (20). Artificial crystalline aluminosilicates are now produced as "molecular sieves" for gas absorption, and the ion-exchanging properties of one of these has been studied by Barrer & Meier (21). With the help of x-ray diffraction they find the structure to contain two types of exchange sites whose size and location impose restrictions on the size and charge of entering ions. Quaternary ammonium ions larger than $(CH_3)_3NH^+$ are "screened out."

The new field of fused salt chemistry offers possibilities for the use of in-

organic ion exchangers of all kinds. Ions of transition metals and the actinides have been absorbed on activated alumina columns from a molten $LiNO_3$-$KNO_3$ eutectic and eluted by adding chloride to the melt [Gruen, Graf & Fried (22)]. Since the solvent itself is highly ionized, this may not be ion exchange in the usual sense of the term; yet, given the selectivity which most inorganic exchangers possess, an ion exchange process is quite conceivable. Certainly this is a promising field for further research.

The new inorganic ion exchangers are already finding applications as catalysts [Austerweil (161)].

*Clays and zeolites.*—Ion exchange in clay minerals was reviewed in an article by Amphlett (23) with special reference to decontamination of radioactive wastes by clay. The same author has measured exchange isotherms for sodium and ammonium ions against cesium ions on a greensand soil and evaluated standard free energies for the exchanges (24). The values are similar to those found previously on attapulgite clay by Merriam and Thomas. The heterogeneity of attapulgite clay as an ion exchanger was shown by the adsorption of butylamine vapor; Chessick & Zettlemoyer measured adsorption-desorption curves over a range of temperatures and evaluated the free energy and heat of adsorption as a function of the amount adsorbed (25). A small proportion of the adsorption sites have a relatively high heat of adsorption.

Slabaugh & Kupka have studied the displacement of calcium ions in calcium montmorillonite by the cations of various primary and secondary amines (26). The uptake of amine becomes less favored, the more amine is absorbed; and this effect is greater the greater the molecular weight of the amine. Similar studies with primary amines and montmorillonite were reported by Cowan & White (27) and by Sieskind & Wey (28). The latter workers find adsorption by van der Waals' forces which increases with the chain length of the amine.

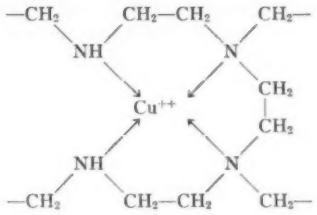
The electrostatic fields created when divalent ions are substituted for univalent ions in a clay with widely spaced negative charges are discussed by Weiss (29). They can cause binding of small anions as well as shrinkage of the clay.

## Organic Ion Exchangers

*New resins.*—A new type of strongly basic anion exchanger was described by Lindenbaum, Boyd & Myers (30). It is made by reacting thionyl chloride with anisol and condensing the product with formaldehyde, and contains tertiary sulfonium ions. Not all of the sulfur is in this form, however, as the ion exchange capacity is only half what would be expected. The resin takes up tracer amounts of Fe(III) and Zn from solutions of hydrochloric acid and lithium chloride in much the same way that a quaternary ammonium resin does.

Polyethyleneimine which is crosslinked by ethylene dichloride takes up cupric ions from solution to give a resin which is a considerably stronger base

than the original imine resin [Nonogaki *et al.* (31)] and probably contains chelated cupric ions:




The interesting feature of this resin is that its exchange sites are doubly charged. By introducing Co(III), triply charged sites are obtained.

Another interesting anion exchanger was made by Richter & Woermann (32), who partially quaternized polyvinylpyridine with dodecyl groups. The dodecyl groups tend to aggregate within the resin to form micelles, just as in aqueous solutions of colloidal electrolytes. An effect analogous to a critical micelle concentration is found, for the aggregation is sensitive to the degree of swelling of the resin. This in turn can be controlled through neutralization of the weakly basic groups.

Turning to cation exchangers, Wiley & Schmitt (33) prepared sulfonated polystyrene crosslinked with di-(*p*-vinylphenyl)-sulfone, and found it to exchange monovalent ions more than twice as fast as conventional sulfonated polystyrene resins. Phosphate and phosphonate resins have been prepared by Lane (34) and by Kennedy *et al.* (35). A phosphorylated cellulose was described by Head *et al.* (36). This has a high affinity for ions of thorium, zirconium, titanium, and uranium; and the authors suggest that the selectivity is due to the flexibility of the cellulose chain which gives freedom of orientation and hence the possibility of chelation. Absorbents selective for uranium have been made by incorporating alkyl pyrophosphates and orthophosphates into cocoanut charcoal [McClaine, Noble & Bullwinkel (37)].

Amphoteric resins have been prepared, containing both basic and acidic groups. These could have chelating properties and hence a certain selectivity. Phosphonamide and aminophosphonate polymers were made by Kennedy & Ficken (38); a hydroxamic acid resin, selective for iron, was made by Cornaz, Hutschneker & Deuel (39a). A resin containing basic nitrogen atoms and sulfonic acid groups was described by Davankov *et al.* (39). These authors discuss such "secondary properties" of resins as their catalytic and coagulating ability, with special reference to the recovery of precious metals by ion exchange resins. Redox resins and their ability to produce hydrogen peroxide from air and water were discussed by Manecke & Bahr (40).

*General properties of organic exchangers.*—The chemical and physical structure of ion exchange resins has received much attention in the Soviet Union. Apparently a wide range of resins is commercially available. The properties of 27 of these resins were summarized by Saldadze & Demonterik

(41), with information on the effects of such oxidizing agents as air, hydrogen peroxide, chlorinated water, and nitric acid. Many of the Russian resins are condensation products which are sensitive to chemical attack and contain low molecular weight material. The drawbacks of polycondensed products compared to polymerized products were discussed by Losev & Trostyanskaya (42), and by Vasilyev (43). These authors also discussed the chemical breakdown occurring during sulfonation and nitration of styrene polymers. Trostyanskaya & Tevlina (44) and Davankov & Laufer (45) discussed the suitability of various ion exchange resins for use in the food and pharmaceutical industries. Crumbling of ion exchange resin granules and its prevention was discussed by Meleshko *et al.* (47).

The thermal stability of sulfonic acid resins (sulfonated polystyrenes, as well as phenolsulfonic acid resins) was investigated by Vasilyev (46), who measured the rates of hydrolysis of $RSO_3H$ to RH plus $H_2SO_4$ at various temperatures. The production of sulfuric acid and carbon dioxide by hydrogen peroxide attack on various sulfonic acid monomers and polymers was measured by Hookway & Selton (48). They showed that crosslinking of polystyrene sulfonic acids greatly reduced the chain degradation and carbon dioxide production.

Drozdov & Popov (49) reported a study of the sulfonation of coal, using fuming sulfuric acid labelled with $S^{35}$. They showed that the sulfonic acid groups in the product come entirely from the sulfuric acid, not from the sulfur originally present in the coal; in fact, some of the original sulfur is lost during sulfonation.

*The heterogeneity of ion exchange resins.*—That condensation type resins are inhomogeneous is not surprising. A paper by Koschel & Schlögl (50) cited in last year's review shows clearly that a phenosulfonic acid-formaldehyde resin mass contains islands of tightly crosslinked material surrounded by more weakly crosslinked material. It is now evident that sulfonated polystyrene resins are heterogeneous too. Chen & Hammett (51) prepared copolymers of esters of styrenesulfonic acid and hydrolyzed them partially to give a series of resins with differing proportions of free sulfonic acid groups. They found that the first sulfonic acid groups to be liberated in the resins by hydrolysis were more catalytically active than those liberated later on. There seemed to be a great difference in the accessibility of the sulfonic groups, suggesting that some lay in loosely crosslinked regions and others in tightly crosslinked regions within the same resin bead.

Differences between individual beads of the same resin batch were found by Högfeldt (52). He measured the silver ion-hydrogen ion exchange equilibrium on single beads of a sulfonated polystyrene-divinylbenzene copolymer with four per cent nominal crosslinking, using radioactive silver. The distribution constants varied over a range 2.6:1 between different beads. The swelling of the beads varied in a parallel manner. Whether this heterogeneity is characteristic of all resins of this type is another matter. Flotation measurements by the reviewer would suggest that most commercial resins are more homogeneous than this.

## Thermodynamic Studies of Ion Exchange

*The exchange of simple ions.*—Cruickshank & Meares (53) have published a detailed thermodynamic treatment of the three exchanges, $K^+$-$H^+$, $K^+$-$Cs^+$ and $K^+$-$Sr^{++}$, in a sulfonated polystyrene with 10 per cent crosslinking. They measured heats of exchange calorimetrically as well as the exchange equilibria. From their data, together with appropriate data for the chloride solutions used, they evaluated "excess" enthalpies, free energies, and entropies of exchange, that is, quantities in excess over what would have been found had resins containing two cations behaved as ideal solid solutions. The results for the $K^+$-$Cs^+$ exchange were particularly revealing, inasmuch as the equivalental swollen volumes of the $K^+$ and $Cs^+$ resins are practically identical, and changes in hydration energy and in network configurational entropy would have a negligible effect. Yet the distribution quotient varied considerably with resin composition. Cesium was the preferred ion, and the preference of the resin for cesium increased with increasing proportion of cesium in the resin; the distribution quotient rose by a factor of nearly 10 over the complete composition range. The excess equivalental enthalpy, meanwhile, varied in a peculiar manner. The authors concluded that the nonideality of this system is a result of nonrandom mixing of the two cations. Unhydrated cesium ions are considerably larger than unhydrated potassium ions, suggesting that the imperfect mixing is due to local variations of crosslinking within the resin beads.

The volume changes accompanying ion exchange have been analyzed by Högfeldt (54). On the assumption that the partial molal volume of water in the resin remains constant, he evaluated the partial equivalental volumes of the potassium and tetramethylammonium ions in resins of three different crosslinkings, using data by Gregor. Högfeldt noted that the difference between the two equivalental volumes decreased linearly with the total molality within the resin.

The heats and free energies of water absorption by crosslinked sulfonated polystyrenes in the hydrogen form were measured by Lapanje & Dolar (55). They found these quantitites to depend primarily on the molal concentration in the resin, and only to a minor degree on the crosslinking. The relation between swollen volume, ionic radius, and ion exchange selectivity was explored by Meleshko & Myagkoi (56). Samsonov *et al.* (57) related the swelling of different sulfonic and carboxylic resins with the $Na^+$-$Ca^{++}$ equilibrium in these resins. Swelling in water-alcohol mixtures was studied by Samuelson (58). Heats of exchange of several cations against hydrogen ions were measured by Zapior & Leszko (59), and correlations with charge and ionic radius were found. A general discussion of the thermodynamics of exchange in terms of electrostatic effects in the resin and ion-solvent interactions, supported by equilibrium data in water-methanol mixtures, was given by Gorshkov & Panchenkov (60). Davydov (61) studied the chloride-nitrate exchange in water-ethanol mixtures.

The gathering of data on ion exchange equilibria continues, though the

interpretation of the more complex exchanges remains very puzzling. Bonner & co-workers (62) have presented more equilibrium data for divalent and trivalent cations; Erickson (63) studied the $Nd^{+3}-H^{+}$ exchange. The binding of several divalent and trivalent ions by a sulfonic exchanger was studied by Golovatyi (64). Saldadze (65) included trivalent ions in an extensive study of equilibrium distributions in resins and clays, and concluded that the activity of an ion in an exchanger was closely proportional to its equivalent fraction in most cases. The uptake of amino acids by cation exchange resins in the hydrogen form was discussed by Samsonov & Kuznetsova (66), who concluded that two mechanisms were involved and that amino acid dipoles could be absorbed.

*The exchange of complex ions.*—Aveston *et al.* (67, 68) have measured the absorption of the aurocyanide complex ion, $Au(CN)_2^-$, by strongly and weakly basic anion exchange resins. This ion is highly polarizable and hence very strongly absorbed, even by weakly basic resins in alkaline solutions, where such resins would normally not bind anions at all. Ion pairs are believed to be formed in these cases. In strongly basic resins the singly charged, highly polarizable ion $Au(CN)_2^-$ readily displaces divalent ions whose polarization is presumably reduced by stretching between two resin cations. The ability of singly charged anions to displace $Au(CN)_2^-$ is directly related to their polarizability as measured by ionic refraction. Thus $I^-$ is more strongly attracted than $Br^-$, and $ClO_4^-$ than $BF_4^-$ (68).

Bromine and iodine are absorbed from solutions by a strongly basic anion exchange resin containing chloride, bromide, or iodide ions [Aveston & Everest (69)]. Bromide resin absorbs bromine to form the ion $Br_7^-$, and iodide resin plus iodine forms $I_7^-$. The stabilities of these ions in the resin is perhaps due to their polarizability.

The structure and stability of complex ions within ion exchange resins has been studied by Cockerell & Woods (70, 71). They showed that titanium (IV) was absorbed by a strongly basic resin from solutions of hydrofluoric acid, and that the absorption reached a sharp maximum at a moderate fluoride ion concentration. The titanium species absorbed was probably $TiF_5^-$, but this could not be stated unequivocally. Copper (II)—oxalate complexes were absorbed on a strongly basic resin; as the ratio of oxalate to copper in the solution increased, the oxalate to copper ratio in the resin rose to a value 6:1 and higher. The evidence clearly showed that a complex $Cu(HC_2O_4)_6^{-4}$ existed in the resin (70). The pH of the external solution was between 7 and 9, and the concentration of free $HC_2O_4^-$ ions was negligible. Thus it seems that the high electric fields in the resin can stabilize ions which would otherwise hardly exist.

In this connection the data of Nelson & Kraus (72) on activity coefficients of electrolytes in the resin phase are of interest. They measured the absorption of various electrolytes (HCl, LiCl, NaCl, $H_2SO_4$, $BaCl_2$, $CaCl_2$) by a strongly basic resin. The mean activity coefficient in the resin was generally less than in the solution and sometimes much less, especially with dilute (0.1

molar and less) solutions of sulfuric acid. It seemed that the dissociation of $HSO_4^-$ was much less in the resin than in the solution. This is, of course, true of weakly basic resins, which tend to bind sulfuric acid as $HSO_4^-$. The absorption of HCl was measured for a series of quaternary base resins of different crosslinking, and a relation found between the mean activity coefficient of HCl and the total ionic concentration in the resin.

The uptake of zinc as its chloride complex by a strongly basic resin was studied by Horne (73) with a view to elucidating the effect of the cation on the absorption. It is known that anion exchange resins absorb metal ions quite differently from hydrochloric acid solutions than from lithium chloride solutions, for example. This shows that the chloride ion concentration in solution is not the only factor determining the absorption of the metal chlorocomplex, nor is the activity coefficient of the chloride salt. Horne measured the absorption of tracer quantities of zinc from solutions of different quaternary amine salts and concluded that ion pair formation is involved.

Saldadze *et al.* (74) studied the uptake of $Zn^{++}$, $Cu^{++}$, and other divalent ions by weakly basic anion exchangers containing primary, secondary, and tertiary amine groups. These ions co-ordinate with the amine groups of the resin, as they would with such amines in solution. Apparently two amine groups are attached to each metal ion. These complexes are broken down by hydrochloric acid and the metal is extracted, although it may be readsorbed at higher acid concentrations if a stable chloride complex is formed. This is the case with cadmium.

*The determination of complex ion stabilities in solution.*—Ion exchange equilibrium has become an established technique for measuring the dissociation of complex ions in solution. The assumption is made that, under the conditions of the experiment, only the simple hydrated metal ion enters the cation exchange resin and that its complexes do not. This is a reasonable assumption when complexes of a metal with anions are considered. The stability of Co(II) and Zn(II) oxalate complexes was measured by Schubert *et al.* (75), who proved that no oxalate entered the cation exchange resin by using $C^{14}$-labelled oxalate. They also measured the stability of glycolic and citric acid complexes of these metals.

By equilibrating solutions with both anion and cation exchange resins, more information can be obtained about the complexes present. The complexes of Tl(I) and Tl(II) with $OH^-$ and the halide ions were studied in this way by Horne (76), uranyl-phosphate complexes by Marcus (77), and aluminum-phosphate complexes by Salmon & Wall (78). The last-named workers found evidence of polynuclear cationic complexes, and they also showed cationic sulfate complexes of aluminum to exist. The aluminum complexes were less stable than the corresponding ferric complexes.

A thorough discussion of this method of studying complex ions was given by Nikolsky (79). He investigated the interaction of zirconium ions and nitrate ions in perchloric acid solutions, and showed that an anionic nitrate complex is formed; in 2N perchloric acid alone, the species $Zr^{+4}$ predominates.

Uranyl ions and acetate ions associate in sodium perchlorate solutions to give neutral and negatively charged species but not $UO_2(OAc)^+$. By this technique, the presence of neutral colloidal species (such as colloidal hydroxides) can be detected where it occurs.

The absorption of tellurate ions by a quaternary base resin in the chloride form was studied by Everest & Popiel (80). Below pH 8.5 polynuclear complexes are absorbed; at pH 4.5, nearly three tellurium atoms are absorbed by the resin for every choride ion displaced. Ions such as $Te_3O_{10}^=$, $Te_4O_{13}^=$ and $HTe_4O_{13}^-$ are postulated.

Some of the transition metals form complexes which are sufficiently slow to decompose that they can be absorbed and separated on an ion exchange column. The charge per metal atom can then be determined from the maximum uptake, the charge per ion from equilibrium measurements. In this way Cady & Connick (81) showed the existence and constitution of cationic ruthenium-chloride complexes.

*Nonelectrolytes in ion exchange resins.*—The partition of water and polyhydric alcohols between resins and solutions was studied by Mattison & Samuelson (82), who also measured the uptake of these alcohols as a function of the exchangeable ions of the resin (83). Both anion and cation exchange resins were used. As would be expected, the more strongly hydrated ions, such as $Li^+$, tended to attract water into the resin at the expense of the alcohol; but, in nearly water-free solutions, a potassium resin took up twice as much glycerol as did a lithium resin. The alcohols studied were absorbed in the order glycol <glycerol <sorbitol, mannitol. These workers used resins with eight per cent crosslinking and less. Clark (84), on the other hand, using a 12 per cent crosslinked sulfonated polystyrene resin and a column technique, found that sorbitol was most excluded by the resin, then glycerol, then glycol. He used this fact to separate glycerol from other polyhydric alcohols by an ion exclusion technique.

## Diffusion and Kinetic Studies

A knowledge of diffusion rates in ion exchangers is important for interpreting the rate of ion exchange and the behavior of ion-exchanging membranes. The simplest kind of diffusion measurement is that of self-diffusion, in which ions of a radioactive tracer change places with inactive ions of the same element. Interdiffusion, where one ion moves in one direction while another ion moves in the opposite direction, is a more complex affair because the two ions will not have the same mobility and may have different charges; yet this is what takes place when one ion replaces another in a resin bead.

Helfferich (85) and Helfferich & Plesset (86) have tackled the problem of interdiffusion of two ions of equal charge in a spherical resin bead. When one ion tends to diffuse faster than the other, an electrical potential gradient is produced which holds back the faster ion and accelerates the slower ion. By setting up the Nernst-Planck equations, which give the ion fluxes in terms of concentration gradients and electrical potential gradients, and combining

these with the requirements of over-all electroneutrality and zero current flow, the flux of the moving ions can be expressed in terms of the concentration gradient and an interdiffusion coefficient whose value depends on the ratio of the concentrations of the two ions. The problem is one of nonlinear diffusion and has to be solved by numerical integration. Using a computer, the authors calculated the degree of attainment of equilibrium as a function of time for different ratios of the two individual diffusion coefficients, and also the concentration profiles within the resin bead. Equilibrium is reached faster when a fast-moving ion, A, is originally in the resin and exchanges with a slow-moving ion, B, in the solution than when the positions are reversed and B is initially in the resin being displaced by A from the solution (86). A different treatment of interdiffusion is given by Beattie & Davies (87).

Data which could provide a test of these calculations were provided by Dickel & Grimmeiss (88). They measured the rate of reaction of a sulfonated polystyrene resin, initially containing hydrogen ions, with solutions of alkali metal chlorides of various concentrations. With concentrations above 1 *N* the exchange rate was controlled by particle diffusion. Cesium chloride gave the fastest exchange, LiCl the slowest. In view of Helfferich's calculations it is unfortunate that they did not start with the alkali metal ions in the resin instead of hydrogen ions. Follenius & Platzer (89) have described a microscopic technique, using interference fringes, which makes possible the study of concentration profiles in resin beads during ion exchange.

The self-diffusion rates of sodium and bromide ions in a phenosulfonic resin were measured by Schlögl & Stein (90). It is relatively easy to make diffusion measurements in resins of this type, because they can be produced in the form of membranes or rods. Two types of measurement were made, one in which the ions diffused from a solution with radioactively labelled ions across a resin membrane into a solution with inactive ions at the same concentration, and another in which a cylindrical rod of resin was impregnated with radioactively labelled ions and dipped into a solution containing nonradioactive ions. In the first experiment the tortuosity of the diffusion paths, or channels, affects the rate; in the second, it does not. In both experiments the self-diffusion of bromide ions was much faster than that of sodium ions, especially at low temperatures. The "tortuosity" for sodium ions was also considerably more than for bromide ions. It seems that the sodium ions have to move from one fixed sulfonate ion to another along the walls of the "channels," while the bromide ions can pursue a straighter path down the middle of the "channels." It should be noted that the resin had a high water content. The inhomogeneity of the resin (50) probably influenced the results also.

Similar results were found by Meares (91) who studied the self-diffusion of sodium and chloride ions across a disc of phenosulfonic resin. As long as the external concentrations were small, compared to the concentration of the fixed ions in the resin, the diffusion rate of the sodium ion was about half its normal value (after making allowance for tortuosity), whereas the chloride ion diffused at its normal rate in aqueous solutions. Jakubovic, Hills & Kit-

chener (92) measured self-diffusion rates of sodium and cesium ions in phenolsulfonic resins with different degrees of crosslinking. The diffusion rates were considerably less than the theoretical (based on diffusion rates in water and the tortuosity of the resin) for low crosslinked resins but approached the theoretical rates as the crosslinking was increased. The picture of the cation migrating from one fixed ionic group to another along the polymer chains seems to be a good one. It is supported by the work of Dux & Steigman (93) on the self-diffusion of strontium ions in aqueous solutions of polystyrene sulfonic acids.

The rates of diffusion of various salts across a phenosulfonic resin membrane were measured by Romankevich *et al.* (94). The order of the rates does not parallel the order in aqueous solutions, and suggests that specific resin-cation attractions may be present. A theory of diffusion rates of salts across ion exchanging membranes was given by Oel (95).

## Ion-Exchanging Membranes

*Electrochemistry.*—The electrochemistry of ion exchanging membranes was reviewed by Sollner (95a). The text of a lecture by Schmid (96) summarizes his well-known work in a lucid way. Schmid's approach is to treat the membrane as a homogeneous phase having a certain concentration of fixed charges, and to use the Donnan equilibrium to relate the concentrations of mobile ions in the membrane to the concentrations of these ions in the external solution. All concentrations are considered to be sufficiently low that ideal solution laws can be used. Schmid illustrated the use of the model by calculating the electro-osmotic effect, and was careful to emphasize its limitations.

A more general treatment of transport processes in ionic membranes is that of Spiegler (97). He considers the membrane to contain irregular channels a few molecular diameters wide, with fixed negative charges on the walls and sodium ions, chloride ions, and water molecules within the channels. Each of the mobile constituents is subjected to a generalized force, with electric, hydrostatic, and diffusional components. In steady flow this force is opposed by a "frictional" force which is assumed to be proportional to the velocity, and depends on interactions of the mobile species among themselves and with the walls. The equations of motion are simplified by introducing the principle of microscopic reversibility. Spiegler showed how the interaction coefficients can be calculated from experimental data. The model gives plausible values for frictional coefficients and electro-osmotic water transport, and is a distinct advance on the familiar Helmholtz-Smoluchowsky capillary tube model.

A new technique for preparing membranes was described by Gregor & Wetstone (98). They dissolved polystyrenesulfonic acid along with a vinyl chloride-acrylonitrile copolymer in dimethylformamide and evaporated the solution, obtaining an insoluble film whose ion-exchanging properties were similar to those of crosslinked sulfonated polystyrene. Polycarboxylic acids

could be incorporated into films in the same way. Bi-ionic potentials were measured across these films and the mobilities of various cations, including $K^+$, $Ca^{++}$, and $Cu^{++}$, were compared.

Freise (99) studied the copper ferrocyanide membrane and found that, when first formed, it had cation-exchanging properties and showed bi-ionic potentials. This was a metastable condition, however; the membrane eventually lost its ionic selectivity but retained its selectivity for water.

*Applications.*—The applications of ion-exchanging membranes as indicator electrodes in analysis continue to be explored [Parsons (100)]. A design for a continuous flow, multicompartment electrolytic desalter using ion-exchanging membranes was described and quantitatively discussed by Partridge & Peers (101). Peers (102) discussed the separation of amino-acids from sodium chloride by electrodialysis, giving experimental data and optimum working conditions for a three-compartment cell. Similar work was reported by DiBenedetto & Lightfoot (103).

Ion-exchanging membranes have found uses in preparative chemistry to aid electrolytic reduction. Thus uranium (VI) is reduced at a mercury cathode to uranium (IV) in a cell compartment bounded by a cation exchange membrane, which prevents the entry of unwanted anions. The compounds $UF_4$ [Higgins *et al.* (104)] and $NH_4UF_5$ [Schulz *et al.* (105)] have been prepared in this way. The first of the publications just cited (104) describes a complete process for treating uranium ores by acid leaching followed by continuous ion exchange.

These membranes can be used to control the migration of ions in primary cells, such as the alkaline silver peroxide-zinc cell [Bieber, Bruins & Gregor (106)].

## Separations by Ion Exchange

The great majority of publications on ion exchange are concerned with separations performed for preparative purposes, for purifications, or for analysis. To review all these publications would be a prodigious task and, in a review of physical chemistry, an unnecessary one. It is hoped that the choice of papers made below is representative.

*Column theory.*—A short paper by Glueckauf (107) discussed the theory of separations by elution chromatography with reference to separation of isotopes. The theory was applied to data on the separation of the sodium isotopes, $Na^{22}$ and $Na^{24}$, at various temperatures. Values for the heat and entropy of the exchange were calculated.

An approximate method for the calculation of elution and displacement chromatograms was described by Rachinsky (108). A laminar method was used which is applicable to nonequilibrium conditions. The prediction of column performance from the results of equilibrium shaking tests was discussed by Mann (109) and the method applied to the elution of macro quantities of lead by dilute nitric acid. The use of adsorption isotherms in choosing conditions for uptake and elution in column operation was discussed by

Izmailov (110) in connection with a multicolumn continuous flow process for recovering alkaloids. Anokhin (111) discussed column dynamics and its relation to equilibrium and kinetic data.

*General analytical techniques.*—Yoshimura & Waki (112) described a comprehensive scheme for silicate rock analysis in which the solution containing the metallic constituents is treated with a quaternary base resin in presence of three different concentrations of hydrochloric acid. This gives a preliminary sorting. The three fractions are then passed through cation exchange resin columns and further resolved by selective elution. Reichen (113) used cation exchange to separate sodium and potassium from the elements in silicate rock analysis. A combination of anion exchange and complexing with ethylene diamine tetraacetic acid was used by Newman (114) to separate fluoride from phosphate rock; $F^-$ was eluted from the anion exchange resin column by an ammonium chloride-ammonia buffer while phosphate ions and anionic metal complexes remained. Nielsen (115) used a quaternary base resin in the acetate form to concentrate microgram quantities of fluoride in the analysis of animal tissue.

Traces of potassium ions were removed from solutions and also from suspensions of ground mica, by shaking with pieces of cation exchange resin membrane [Zemany, Welbon & Gaines (116)]. The membranes were then examined by x-ray emission spectroscopy to determine the potassium. Traces of iron were removed from solutions of ammonium phosphate and of alkaline earth salts by adding 2,2′-dipyridyl and absorbing the resulting ferrous complex on a cation exchanger [Witzmann & Hahn (117)]. This was done, not to determine the amount of iron, but to purify the solutions for the preparation of phosphors. The van der Waals' attraction between the dipyridyl groups and the aromatic groups of the exchanger undoubtedly contributed to the success of this technique. A combination of complex formation and ion exchange was also used by Golovatyi (118) to remove iron (III) from solutions of salts of magnesium, aluminum, zinc, copper, and nickel.

Yamatera (119) showed that tracer quantities of metals can be selectively eluted from ion exchangers by reagents which tend to precipitate them. Thus cesium could be selectively eluted by perchloric acid.

*Separation of specific elements.*—The ion exchange extraction of uranium in ore processing continues to receive attention. A recent symposium was briefly reported [Greer *et al.* (120)]; reference has already been made to the work of Higgins *et al.* (104). Most ion exchange recovery of uranium is done by anion exchangers from dilute, acidic sulfate solutions; however, strong base ion exchangers also take up uranium from carbonate leach solutions. Poirier *et al.* (121) used this fact in a process for extracting uranium from monazite sand. Certain complexing anions, in particular nitrate and chloride, interfered strongly. Another ion exchange process for obtaining uranium from monazite sand was described by Barghusen & Smutz (122).

Selective elution from a cation exchange resin column was used by

Samedy (123) to separate uranium, iron, zirconium, and thorium. They were eluted in that order, the first three by hydrochloric acid of increasing concentration, the last by the disodium salt of ethylene diamine tetraacetic acid. Elution of thorium from a cation exchanger by $3M$ sulfuric acid was used by Nietzel, Wessling & DeSesa (124), who employed both anion and cation exchange in a scheme for the analysis of thorium ores. The stability of the thorium-sulfate complex anion also permits selective absorption of thorium on an anion exchange resin [Nagle & Murthy (125)].

The traces of protoactinium which occur in equilibrium with uranium were separated from a large amount of uranium by Kimura *et al.* (126). Improvements in rare earth separations were reported by Wolf & Massone (127), by Brunisholz (128), and by Loriers & Lenoir (129). These last workers used displacement chromatography on a column of cation exchange resin bearing cupric ions. Since cupric ions are complexed by the same reagent which is used to complex the rare earths, they are displaced much more readily than the ammonium ions usually used, and a sharper band front results. The process is suitable for large-scale separation.

Zirconium and niobium were separated by cation exchange with successive elution by complexing agents [Sano & Shiomi (130)], and scandium, titanium, and vanadium were separated on an anion exchange column by using the differing stabilities of their oxalate complexes [Walter (131)]. Anion exchange in hydrofluoric acid was used to recover carrier-free vanadium, scandium, and arsenic from cyclotron targets [Schindewolf & Irvine (132)].

Separation of the platinum metals was discussed by Berman & McBryde (133, 134). They measured the distribution coefficients of Ru, Rh, Pd, Ir, and Pt between hydrochloric acid and a quaternary base resin. The data were interesting in themselves and guided the development of separation processes. Marks & Beamish (135) adapted Berman and McBryde's procedures to a method for separating microgram amounts of rhodium and iridium from a large excess of base metals. A study of complex ions of rhodium (III) using paper chromatography and ion exchange was described by Shukla (136).

The uptake of gold by anion exchange resins was discussed above (68). An analytical method for gold which uses ion exchange was discussed by Ezerskaya & Markova (137). Davankov, Laufer & Shits (39) discussed gold and silver recovery using the "secondary" properties of ion exchange resins (reducing and coagulating power).

Beryllium was separated from other metals, including uranium, by cation exchange [Schubert, Lindenbaum & Westfall (138)]. Microgram amounts of zinc were separated from ashed plant materials by anion exchange in hydrochloric acid solutions [Maier & Bullock (139)]. The absorption of zinc and other metals by anion exchangers from hydrochloric acid solutions is much improved by adding acetone or ethyl alcohol; this effect was studied by Yoshino & Kurimura (140). Berg & Trumper (141) separated zinc, cad-

mium, and mercury by anion exchange, using 0.01 *M* hydrochloric acid in 25 per cent methanol to separate Zn and Cd. Cadmium was separated from zinc concentrates by absorbing the stable anion $CdI_4^=$ [Kallman *et al.* (142)], and cadmium was separated from lead, bismuth, and copper by absorbing all the metals on a cation exchanger, then eluting all except the cadmium by a sodium hydroxide-glycerol solution [Kreshkov & Sayushkina (143)].

An elution separation of iodide, iodate, and periodate ions was described by Good, Purdy & Hoering (144).

*Applications to organic compounds.*—An improved technique for separating amino acids was reported by Hamilton (145). He showed that restricting the range of particle size of the resin made the elution bands sharper, particularly when high flow rates were used. He described a flotation technique for fractionating resin particles in the size range 10 to 60 $\mu$. Further data on amino acid separation were reported by Moore, Spackman & Stein (146). Fractionation of the proteins in egg white was described by Rhodes, Azari & Feeney (147), who used carboxymethylcellulose as the ion exchanger.

Where organic compounds are used with resinous ion exchangers the possibility of nonionic binding is always present. It is particularly likely to occur with compounds containing aromatic rings. Watkins (148) showed that pyridine, aniline, and benzylamine were absorbed from water solutions by sulfonated polystyrene resins in excess over the ion exchange capacity of these resins. In solvents such as glacial acetic acid, however, this was not the case. Changing the solvent makes a great difference to the binding of organic ions by exchangers, and separations which work well in one solvent are poor in another. Aniline and pyridine could be eluted in successive bands from a cation exchanger by hydrochloric acid in methanol or ethanol, but in water the bands overlapped (148).

The absorption of alkaloids by ion exchange resins is fairly easy, but elution is difficult. The use of a very weakly crosslinked resin was described by Berggren *et al.* (149), and the use of butanol as a solvent in morphine recovery by Brekke *et al.* (150). Morphine can be separated from codeine by ion exchange [Shemyakin & Karpov (151)].

Polysaccharides, such as pectin, were fractionated by Steiner, Neukom & Deuel (152) using colloidal anion exchange resins in the chloride form. The separation of phosphorylated sugars [Wright & Khorano (153)] and organophosphate insecticides [Plapp & Casida (154)] were described.

*Ion exchange in paper chromatography.*—Filter papers impregnated with colloidal ion exchange resins are now available. Using the conventional techniques of paper chromatography, some interesting separations have been achieved. Copper and cadmium, uranium, iron, thorium, and aluminum have been separated on cation exchange resin-impregnated paper by using dilute hydrochloric acid as developer [Lederer (155)]. Organic acids, including fruit acids and amino acids, have been separated on anion and cation resin papers [Myhre & Smith (156)]; Tuckerman (157) separated amino acids also.

A paper chromatography technique called "focussing ion exchange" was

described by Schumacher & Streiff (158). The metal ions to be separated are placed in the middle of a broad strip of paper. One end of the strip dips into a solution of a complexing agent such as the disodium salt of ethylene diamine tetraacetic acid, the other end dips into a solution of a strong acid. The solutions mix by diffusion along the length of the paper, producing a concentration gradient of complexing ions; complexing power is almost zero at the acid end and maximum at the other, alkaline end. An electric field is now applied with the negative pole at the alkaline end, the positive pole at the acid end. The uncomplexed metal cations move one way along the strip, the complexed metal anions the other; each metal is concentrated in a narrow band where its ions are roughly half complexed and half free. The position of this band depends on the stability of the complex. Since the ions of the complexing agent are steadily moving under diffusion while the bands stay still, a continuous exchange occurs between the metal ions and the hydrogen ions of the complexing agent. This is, of course, a different kind of ion exchange from that which is the subject of this review.

*Liquid ion exchangers.*—A liquid which is insoluble in water and yet has acidic or basic character can absorb bases or acids from aqueous solutions and exchange ions with such solutions. An example of a "liquid ion exchanger" is a long-chain amine. These amines will take up metal ions from aqueous chloride solutions as negatively charged chlorocomplexes. Since the liquid amine is homogeneous, the physical laws of such a system are simpler than those of solid ion exchangers. The uptake of zinc from chloride solutions was discussed by Schindewolf (159).

## Catalysis

Noller & Hassler (160) studied the acid-catalyzed decomposition of ethyl cyanoacetate by a series of resins having different internal hydrogen ion concentrations. Both the rate of the reaction and its apparent energy of activation decreased as the proportion of hydrogen ions to sodium ions in the resin increased. Diffusion, however, influenced the measured rate of reaction. When allowance was made for this, the true activation energy of the resin-catalyzed reaction was the same as that of the acid-catalyzed reaction in homogeneous solution.

The catalysis of epoxidation by ion exchange has aroused much interest, and Austerweil (161) has shown that acidic inorganic exchangers, such as colloidal zirconium phosphate, make good catalysts because they are stable at the high temperatures needed for the reaction. The addition of water to epoxides to yield glycols is catalyzed by strongly acidic resins; Othmer & Thakar (162) studied the variables in this process. Mastagli & Lagrange (163) used a strongly acidic cation exchange resin and a strongly basic anion exchange resin together in the same reaction vessel to perform the Knoevenagel synthesis, starting with an acetal. One resin catalyzed the hydrolysis of the acetal to the aldehyde, the other catalyzed the condensation of the aldehyde with ethyl cyanoacetate.

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# TRAPPED ENERGETIC RADICALS[1,2]

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## Introduction

While the entrapment of highly energetic species in solid matrices at low temperatures recently has received a great deal of attention (22, 23, 95, 99, 132), contributions to this field have been made over many years. Dewar (35) studied and discussed the phosphorescence of various solids at low temperatures in 1895 and 1901. By 1924 Vegard (183) was postulating that irradiated solid nitrogen particles were responsible for the auroral afterglow and both Vegard and McLennan & Shrum (127) were conducting extensive research into the nature of solid nitrogen excited by ionizing radiation. In 1941, G. N. Lewis & his colleagues (115, 116) were able to make a penetrating analysis of the effect of ultraviolet light in activating certain aromatic materials in solids.

The present upsurge of interest arises in part from the availability of better instruments and more advanced theoretical methods for research on such systems. No doubt, a great part of this interest also arises from various urgent practical uses to which such systems might be put; greatest of these, of course, is the prospect of obtaining a high-thrust fuel for rocket engines (164, 178). Of almost equal interest are various chemical syntheses which might be possible. The interest also has spread to fundamental research areas of solid state physics and low temperature physics and chemistry. Somewhat surprisingly, frozen free radicals have been of great interest to astronomers and cosmologists, offering possible explanations for certain behavior of comets (36, 37, 82) for the nature of interstellar material (182) and for the origin of the colors on Jupiter (147).

This review attempts to summarize and appraise the state of our knowledge and understanding of trapped energetic radicals as of December 31, 1958. It will be obvious that considerable research remains to be done before an adequate understanding of this subject will be achieved. However, a start has been made and much is being accomplished so that no doubt the next few years will see major developments in this field.

Atoms and free radicals in the gas phase (175) and in solution (191) have been favorite subjects of investigation for large numbers of spectroscopists, kineticists, organic chemists, etc., for many years. Much of this material is useful as a background for a study of trapped radicals and excellent standard works on various aspects of free radicals are available.

In studies of trapped radicals, the radicals are either generated in the

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gas phase and then frozen out on a surface at low temperatures (usually 4–77°K.) or they are generated *in situ* by irradiation of the solid with ultraviolet light or various kinds of ionizing radiation. Radicals are formed in the gas phase by thermal decomposition in a furnace or on a heated filament, by several kinds of electric discharges, and by photolysis (175). The state and concentration of free radicals in the gas phase have been determined by mass spectrometry (121, 165), by emission and absorption spectroscopy (88), by various calorimetric methods (143), by electron spin resonance (56, 95, 170, 193), and by chemical reaction (113, 175). Except for mass spectrometry, these same techniques are used for measuring the radical contents of solids. In addition, magnetic susceptibility offers a promising tool for measuring the radical content of solids (171). Statistical studies of the deposition of radicals in a matrix (75, 100) have been valuable in setting upper limits to the concentration of radicals that might be achieved in this way.

X-ray diffraction has proved a very valuable adjunct to studying radicals in solids by giving necessary information about the crystal structure of the matrix. Much of this work has been done by Peiser, Mauer & associates and includes studies of nitrogen (17), oxygen (16), ammonia (19), and mixtures of hydrazoic acid and ammonium azide (18).

Work at low temperatures requires specially designed Dewars, and most experimenters have designed their own to achieve specific objectives (16, 93). For details the reader is referred to specific research papers. However, Schoen *et al.* (168) have described several glass Dewars, and many of the metal Dewars are patterned after that of Duerig & Mador (40).

Until now by far the greater part of the work on trapped radicals has been devoted to a select few, namely, N, O, H, NH, $NH_2$, OH, and $HO_2$. Methyl has received some attention and several other organic radicals have had very limited study. The remainder of this review will be devoted to various individual radicals.

## Hydrogen Atoms

Hydrogen atoms were first produced thermally by Langmuir (111) who studied the dissociation of hydrogen on a hot filament. Wood (195) showed that hydrogen at low pressure (0.2 to 1 mm. Hg) is extensively decomposed to atoms by an electric discharge. Bonhoeffer (20), Geib & Harteck (66), and others have used this method to study reactions of H atoms in the gas phase. The electric discharge method readily produces H atom contents of 50 to 70 per cent. However, H atoms recombine very rapidly on many metal or clean glass surfaces and it is necessary to poison the walls carefully if high atom contents are to be retained. H atoms also disappear by three-body collision in the gas phase (181). Recently Klein & Scheer (108, 109) have used Langmuir's method to produce H atoms and have shown that they react (rapidly, in many cases) with solid olefins at 77°K.

When hydrogen gas is passed through an electric discharge and then condensed at 4.2°K., a very weak glow is observed (11, 22). Although the solid

appears rather different from undischarged hydrogen, there is no evidence that excited species are present in appreciable concentration. However, when hydrogen (condensed at 4.2°K. on a copper rod) was bombarded with canal rays (186), a marked luminescence resulted. The spectrum included 26 lines of which the five most prominent belonged to the Balmer series thus indicating that hydrogen atoms were present. When solid hydrogen was bombarded with cathode rays, a greenish-blue luminescence with a continuous spectrum resulted. Emeleus & Beck (43a) may have trapped H atoms in solid $NH_3$, as indicated by the discoloration of molybdenum oxide caused by gas evaporated from a solid condensed at 90°K. from a discharge through hydrogen and nitrogen.

Convincing evidence of the presence of H atoms in a hydrogen lattice has been obtained by Jen *et al.* (102, 103). They measured the electron spin resonance of both hydrogen and deuterium that had been passed through an electric discharge and then condensed at 4.2°K. Hydrogen gave a doublet and deuterium, a triplet, similar to the gas-phase electron spin resonance spectra of these atoms (14, 68). These lines persisted as long as the temperature remained at 4.2°K. The electron spin resonance spectra gave values of g, and hyperfine coupling constants shifted only very slightly from those for the free atoms, thus indicating that the atoms are very nearly but not quite free in the lattice. In the experiments with hydrogen, several strong lines appeared near the free electron-resonance field. These were grouped in triplet and quartet arrangements. The triplet disappeared when the gas was carefully purified, but the quartet remained (103). The intensity distribution in the quartet was quite asymmetrical and might have been due to $H_3$. In that case, however, a $D_3$ spectrum of seven lines might also have been expected in the same region but none was found. No final explanation could be given. Griffing *et al.* (78) have developed a theoretical molecular orbital treatment of the magnetic properties of linear $H_3$ in an effort to ascertain whether the quartet grouping might arise from this source. The results however are inconclusive.

The first clear evidence that hydrogen atoms can be trapped in solids was found by Livingston *et al.* (119, 120) by irradiating water solutions of $HClO_4$, $H_2SO_4$ and $H_3PO_4$ with gamma rays from $Co^{60}$ at 77°K. Hydrogen atoms were identified by electron spin resonance spectra which agree very closely both in $g_j$ value and hyperfine splitting constant with the values of Jen *et al.* (102). Trammell, Zeldes & Livingston (180) and Zeldes & Livingston (197) in similar studies observed two small satellite peaks near each main peak and attributed these to proton spin flips in conjunction with flips in electron spin resulting from dipole-dipole coupling. Jen *et al.* (103) observed similar satellite peaks for H atoms in a hydrogen matrix and adduced a similar explanation. They considered that, in a hydrogen matrix, the flip in electron spin would cause a change in the parallel nuclear spins of orthohydrogen. Similar results might be expected with deuterium atoms in a $D_2$ matrix, with possible additional transitions due to deuteron-quadrapole

coupling, but the spectrum was not sufficiently resolved to permit conclusions concerning this. Electron spin resonance spectra of H atoms were observed by Wall *et al.* (190) in solid $H_2$ and $CH_4$ at 4.2°K. irradiated by $\gamma$-rays from a $Co^{60}$ source.

When Matheson & Smaller (130) and Smaller *et al.* (173) subjected ice at 77°K. to ionizing radiation they found an electron spin resonance spectrum characteristic of the H atom; $D_2O$ ice gave a characteristic triplet with intensity ratios of 1:2:1. However in both cases splitting is only about 1/16 that of the free atom. They were able to repeat the results of Livingston *et al.* (119) so the difference in hyperfine splitting could not be an instrumental effect. Also their spectra included additional lines that could be attributed (with considerable uncertainty, however) to OH or OD radical. The authors conclude that the small spacing must be attributable to the dielectric constant of the medium which at high frequencies is in the neighborhood of 3. They estimate that a value of 2.5 would account for the effect. It is not clear, however, why similar effects would not be observed in aqueous solutions of acids. Several approximate determinations of the H atom content of the solid have been made. Livingston (117) has measured the $H_2$ evolved when irradiated aqueous solutions of sulfuric and other acids are warmed. The H atom content from the gas measurement agrees well with the value obtained from electron spin resonance determinations. The results depend upon the crystallinity of the medium with maximum values of H atom content in the order of 0.1 per cent. Matheson & Smaller (130) estimated the maximum H atom content of their irradiated ice to be about 0.005 *M* per cent. Jen *et al.* (103) estimated from dipolar broadening that the H atom content of their hydrogen lattice was about 0.01 per cent but pointed out that they had made no effort to maximize this.

### Nitrogen Atoms

Since its discovery by Lewis (114) and Strutt (176), the nature of active nitrogen has elicited a great deal of interest and has been the object of many investigations. A complete review of this field is beyond the scope of this survey, but a brief summary is necessary to provide a background for the studies of the nitrogen system of frozen radicals. Recent surveys are to be found in Evans & Winkler (44), Kurzweg, Bass & Broida (110), and Jennings & Linnett (104).

When an electric discharge is passed through nitrogen at 0.1 to 10 mm. pressure a characteristic yellow glow is observed outside the discharge zone and under the proper conditions this may persist for several hours. The energy carrier of this afterglow has been attributed to various species, but it now seems conclusively proven that the properties of active nitrogen are mainly caused by nitrogen atoms in the $^4S$ ground state. Heald & Beringer (83) studied the electron spin resonance of active nitrogen. Their spectrum was a triplet corresponding to the $^4S$ ground state of N atom. Jackson &

Schiff (98) and Berkowitz *et al.* (15) have allowed active nitrogen from a mild discharge to pass over a pinhole leak which admitted a small amount of the active gas to the ion chamber of a mass spectrometer. By operating at low electron energies both groups found nitrogen atoms to be present in concentrations of 0.1 to 2 per cent. Berkowitz *et al.* (15) showed the afterglow intensity to be proportional to the square of the atom concentration over the pressure range of their experiments. The rate of N atom disappearance has been determined by Herron *et al.* (85) and by Harteck *et al.* (80) using a gas titration technique, by Wentink, Sullivan & Wray (192) from measured heat release, by Young & Sharpless (196) using a Wrede guage, and by Forst *et al.* (55) from studies of the rate of reaction of N atoms in the presence of $CH_3CN$. Both a three body reaction and a pseudo-first order wall reaction are involved and the rate constants for both processes have been determined (85, 192).

Only the first positive bands of $N_2$ are ordinarily observed in emission in the Lewis-Rayleigh afterglow. These arise from the $B^3\Pi_g - A^3\Sigma_u^+$ transition with the 12th, 11th, 10th, and 6th vibrational levels favored. The Vegard-Kaplan bands ($A^3\Sigma_u^+ - X^1\Sigma_g^+$) which are present in the "auroral" afterglow of the upper atmosphere are absent from the Lewis-Rayleigh afterglow. Their absence shows that the comparatively long-lived $A^3\Sigma_u^+$ molecules must be very rapidly deactivated by collision in the normal afterglow. Although atoms in the $^4S$ state are the prevalent atomic species present, Tanaka *et al.* (179) using ultraviolet absorption have observed, in addition to $^4S$ atoms, $^2D$ and $^2P$ atoms in concentrations about 1/500 that of the $^4S$ atoms.

In addition, evidence of one or more unidentified excited species has been accumulated from several sources. Kaufman & Kelso (107) have shown that a large heat effect, as evidenced by a temperature rise of about 100°C., results from addition of a few per cent of $N_2O$ or $CO_2$ to the afterglow. The N atom concentration is not affected. This effect was attributed to excited $N_2$, probably in a low lying vibrational state. From chemical studies, Winkler *et al.* (44, 194) have evidence of an active species other than nitrogen atoms; this species is tentatively attributed to electronically excited $N_2$. Herron *et al.* (85) were unable to detect any excited species with a mass spectrograph but, since the two groups of experimenters employed quite different means of excitation, the latter's failure is not evidence for the absence of the excited species observed by Winkler. Jackson & Schiff (98) also found evidence for an excited state of $N_2$ but Berkowitz *et al.* (15) could not duplicate this.

Perhaps the first studies of excited nitrogen in the solid state were made by Vegard *et al.* (183 to 187) who thought that the auroral afterglow might be caused by the irradiation of solid nitrogen dust in the upper atmosphere. Solid nitrogen at 4.2°K. and at 20°K. was irradiated by Vegard with cathode rays and canal rays. Similar but less extensive studies were made by McLennan *et al.* (125, 126, 127). The spectra of the resulting afterglows were

subjected to extensive analyses by Vegard and many of the bands were correctly assigned to what are now known to be the molecular transitions of $N_2(A^3\Sigma_u^+ - X^1\Sigma_g^+)$ and NO ($A^2\Sigma^+ - X^2\Pi$ and $B^2\Pi - X^2\Pi$).

It was shown by Broida & Pellam (25) that when the gaseous nitrogen afterglow is condensed at 4.2°K. the solid glows with a brilliant green light and with occasional bright flashes as long as the discharge is operating. The glow persists with decreasing intensity for several minutes after the discharge is stopped and reappears upon warming to about 10°K. (53, 141). As the solid is warmed further the green glow decreases and at about 25°K. a less intense blue-green glow is observed. This glow persists to about 35°K. It has been found possible under special conditions to move active species from one surface to another (28). The visible glow, the frequent flashes during deposition, and the occasional violent explosions that have been experienced by various workers in this field attest the fact that the system contains a large amount of trapped energy. Glows of similar appearance have been produced by Hörl (92) using controlled electron bombardment of the solid, by Schoen & Rebbert (169) using an electrical discharge to the solid, and by Wall *et al.* (189) using $\gamma$-irradiation from a $Co^{60}$ source.

The fact that the afterglow in nitrogen gas is due primarily to atomic nitrogen strongly suggests that the energy properties exhibited by the solid may also have their origin in nitrogen atoms. Perhaps the most convincing evidence that N atoms are present is the electron spin resonance measurements of Cole *et al.* (33) and of Foner *et al.* (51). Both groups found a well-resolved triplet with the center line at 2.0005 and 2.002, respectively, and the outer ones split by about $\pm 12$ MC when nitrogen was the matrix. Foner *et al.* (51) also measured the electron spin resonance of N atoms in hydrogen and methane matrices and found a small increase in hyperfine splitting with increasing matrix binding (gas $< H_2 < N_2 < CH_4$). Cole & Harding (32) also measured the electron spin resonance of the products of a microwave discharge in ammonia condensed at 4.2°K. They observed a doublet corresponding to the H atom and a triplet corresponding to N atoms. This splitting is somewhat less than that for N atoms in a nitrogen matrix, whereas in the light of the results of Foner *et al.* (51) one would expect it to be more if ammonia were the matrix. In fact, it seems probable that the ammonia was so extensively decomposed that the matrix was largely a mixture of $N_2$ and $H_2$. Wall *et al.* (189) using electron spin resonance have found the triplet from $N^{14}$ and the expected doublet from $N^{15}$ in solid nitrogen at 4.2°K. irradiated by $\gamma$-rays from a $Co^{60}$ source. They also find the four satellite lines explained by Cole & McConnell (34) as a crystal field effect.

Various estimates have been made of the concentration of trapped N atoms but none is altogether convincing. Broida & Lutes (24), from measurements of the rate of temperature rise of the collection chamber, estimated the N atom content of the solid to be around 0.2 per cent. Minkoff, Scherber & Gallagher (134) measured the heat released during warm-up of the solid nitrogen condensed from the afterglow. Assuming all of the heat to arise from

recombination they computed the N atom content to be about four to six per cent. Since they employed the same means of generating the afterglow as did Herron *et al.* (85) who showed that the N atom content of the gas afterglow was between 1 and 2.5 per cent, the heating results in the solid can only be explained as due to trapping energy in some form other than N atoms, or to an experimental error. This conclusion is reinforced by the reported heat release in the same calorimeter (133) from solids condensed from discharges in rare gases. From magnetic susceptibility measurements, Fontana (54) concludes that a critical concentration near 0.5 *M* per cent N cannot be exceeded in the solid phase of nitrogen condensed from gas discharges. He found that the N atom content built up periodically to as much as 0.5 per cent during deposition, but that these situations were unstable and were followed by the characteristic yellow-green flashes. Coincident with a flash the paramagnetism dropped sharply while the temperature of the solid increased several degrees, indicating a disappearance of N atoms. Jackson (101), on the basis of a simplified model of autoignition, shows that an upper limit of 0.3 per cent atoms is consistent with the properties of the solid. Electron spin resonance measurements (189) indicate the N atom content of $\gamma$-irradiated solid nitrogen to be about 0.03 per cent. Herron (84) has passed the gas vaporized from the glowing solid at low temperatures and pressures into a mass spectometer but has been unable to detect N atoms. From this he estimates the N atom content of the evolved gas stream to be less than about 0.05 per cent. From all of these results we conclude that the N atom content of the solid is probably quite low, not exceeding one per cent. Whether it may be possible to produce a matrix that can entrap N atoms in concentrations of several per cent in a stable situation for prolonged periods is not known but on the basis of current knowledge it seems improbable.

The spectrum emitted by excited solid nitrogen has been extensively studied by Bass & Broida (10), Broida & Peyron (27, 29, 141), and Hörl (92). The most prominent features are a set of five sharp lines ($\alpha$) near 5230 A (blue-green) and three diffuse ones ($\beta$) between 5530 and 5670 A (yellow-green). There are also several less intense molecular systems degraded to the red between 2200 and 6000 A. The $\alpha$ lines were attributed to the $^2D-{}^4S$ transition of N atoms, displaced somewhat by the field of the solid lattice (90). Some of the molecular systems were attributed to $N_2$ and to NO, NH, and $NO_2$ which were present as impurities. The A bands were tentatively attributed (90) to the $^5\Sigma_g^+ - A^3\Sigma_u^+$ transition of $N_2$ resulting from the recombination of two $N(^4S)$ atoms. However, the emitter of these bands is now known to be affected by oxygen and to be independent of nitrogen (141). Thus the mechanism of their formation is not known. When the flow of gas and the discharge are stopped, the spectral lines at 5230 A and two associated groups persist as an afterglow lasting several minutes. All other lines disappeared in less than one second.

Effects of oxygen, water, and hydrogen upon the spectrum of excited solid nitrogen have been studied (29, 141) using high-aperture spectrometers

of considerable resolving power. Removal of oxygen or addition of about 0.1 per cent oxygen did not appreciably alter the intensity of the $\alpha$ lines. With $O_2$ contents greater than one per cent the $\alpha$ lines are suppressed. The $\beta$ lines and A bands were weakened by removal of oxygen and reappeared when 0.1 per cent oxygen was added. With excess oxygen the $\beta$ lines decreased rapidly while the A bands were increasing in intensity relative to the $\alpha$ system. From this it was concluded that $\beta$ is most probably the $^1S_0-{}^1D_2$ transition of atomic oxygen. The upper ($^1S_0$) state is known to have a half-life of about 0.8 sec. in the gas, and during deposition this line disappears in less than 0.1 sec. However, on warming the solid, the $\beta$ and the $\alpha$ lines reappear. Excited oxygen atoms must, then, be produced by chemical reaction during warm-up. Broida & Peyron (29) thought NO might be involved; this seems reasonable since the reaction

$$N + NO \rightarrow N_2 + O$$

proceeds in the gas without activation energy and is sufficiently exothermic to give $O(^1S_0)$.

Dilution of the discharged nitrogen with rare gases (27, 141) reduces the intensity of the $\alpha$ and $\beta$ lines and greatly affects their structure. Most spectacular, however, is the very intense Vegard-Kaplan band system ($A^3\Sigma_u^+-X^1\Sigma_g^+$) which is observed when the argon content of the gas is 80 to 95 per cent.

Recently Peyron *et al.* (142) studied the emission spectrum of excited solid nitrogen in the near infrared. Excitation was accomplished with similar results by either electron bombardment of the solid or by microwave discharge in the gas before deposition. Essentially the same spectra are found by both methods of preparation and many of the spectral features are the same as those reported by Vegard & associates (183 to 187), and by McLennan (125, 126, 127). The $^2P-{}^2D$ transition of atomic nitrogen, shifted about 40 cm.$^{-1}$ towards the red, was observed. This effect is similar in magnitude to that of the $\alpha$ lines. The infrared line had a mean life of less than a second in the solid but reappeared upon warming. Satellite lines on either side of the $^2P-{}^2D$ and of the $^2D-{}^4S$ transitions and separated from the main lines by about 2300 cm.$^{-1}$ have been interpreted (142) as being caused by a triatomic nitrogen molecule $N_2-N$, in which an atom is weakly bonded to a $N_2$ molecule. This interpretation is greatly strengthened by the shifts observed with $N^{15}$. A similar molecule, $N_2-O$, also is postulated on the basis of similar spectral evidence.

The manner in which N atoms are trapped in the solid matrix has been of considerable interest but a completely satisfactory explanation has not yet been published. Milligan, Brown & Pimentel (131) measured the infrared absorption spectrum of the green-glowing solid deposited from a glow discharge at 4.2°K. They observed bands at 2150, 962, and 737 cm.$^{-1}$ which disappeared upon warming to 35°K. and thus appeared to arise from an unstable species. When nitrogen enriched with $N^{15}$ was employed several addi-

tional bands appeared near 2150 cm.$^{-1}$ indicating that this band is attributable to a species involving nitrogen. The authors assign this to the asymmetric-stretching vibration of linear $N_3$ and the 962 and 737 cm.$^{-1}$ bands to possible higher polymers of nitrogen. Brown & Harvey (30) using similar techniques have not been able to reproduce these measurements. However, the probable ($^2\Pi_g$) ground state of $N_3$ does not correlate with the ground states of $N_2$ and N so the $N_3$ radical could only be formed from excited N atoms (58). Nitrogen atoms in the $^2$D state are known to be present and are readily observed by their emission spectrum. They can hardly be present in amounts greater than about one per cent of the N atom content of about 0.02 per cent of the solid. This is a very small amount and would be quite difficult to observe by absorption spectroscopy, and so we consider that the presence of a stable $N_3$ radical is not proved and indeed seems rather doubtful.

Herzfeld (89, 90) has analyzed the emission spectrum of the $\alpha$ lines from the viewpoint that trapped nitrogen atoms are perturbed by the field of the solid. He develops a semi-empirical treatment from these considerations which, when several arbitrary parameters are suitably adjusted, gives good agreement with the experimental data on line splitting, shifts of levels, and the $10^3$-fold reduction in half-life from that in the gas. Herzfeld's treatment (89) pictures the N atom as loosely bound to a neighboring molecule and so placed that a line from the atom to the midpoint of the N—N bond is 2.5 A long and makes a 50° angle with the N—N bond. He considers that the very loose complex that results from his treatment is not the same as that proposed by Milligan *et al.* (131). While this treatment gives a self-consistent picture of the origin of the $\alpha$ lines, it is somewhat unsatisfying in that it does not predict other phenomena. Also, additional recent information (142) on the number of lines and the lifetimes of the $\alpha$ lines show that the detailed model cannot be correct. Further the dimensions of the complex derived from the theory make it too large to fit into the crystal structure of nitrogen. This however is not necessarily serious since the lattice probably contains imperfections which would accommodate such a complex.

Several questions remain unanswered concerning the spectra of the excited solid nitrogen and the manner of disappearance of the nitrogen atoms. Thus, no satisfactory explanation has been advanced for the entrapment of N($^4$S), nor is there any satisfactory evidence for the manner of its disappearance. The nitrogen atoms must, of course, recombine but the spectrum of the solid during deposition and during warm-up shows little evidence of the first positive system which is the principal spectral feature of the gaseous afterglow. However, under some conditions the Vegard-Kaplan ($A^3\Sigma_u^+ - X^1\Sigma_g^+$) bands are observed with great intensity. These bands presumably arise from the recombination of the $^4$S atoms.

### Oxygen Atoms

Oxygen atoms can be produced by photolysis but are probably best produced by an electric discharge (175). The familiar Woods tube has been

used by many experimenters, and microwave discharges have recently been found convenient (11, 106, 107, 162, 163). Herron & Schiff (87) have made a mass spectrometric study of oxygen excited by passage through a microwave discharge at about 1 mm. of mercury. By titrating the gas with $NO_2$ they determined the O atom content to be about eight per cent. They also compared the ion abundance curves of the 32 peak of excited and unexcited oxygen and found about 10 to 20 per cent of excited $O_2$ having an appearance potential about 1 v. below that of ground state $O_2$. This was interpreted as $O_2(^1\Delta_g)$. Using a mass spectrometric method they had previously developed (86), they ascertained that the gas contained less than 0.02 per cent of ozone, which probably means that the ozone was removed by reaction as fast as it was formed. Ozone could be recovered by condensation in a trap at 77°K. downstream from the leak and so must have been formed by reaction during condensation. McGrath & Norrish (124) showed that flash photolysis of ozone results in the formation of ground ($X\Sigma_g^-$) state oxygen excited to as much as the 16th vibrational level. Energy considerations led them to the conclusion that the reaction is probably

$$O + O_3 \rightarrow O_2(^3\Sigma_g^-) + O_2(^1\Delta_g).$$

It is possible that the $(^1\Delta_g)$ state of $O_2$ observed by Herron & Schiff may have come about by this reaction which kept the ozone content low. If so vibrationally excited $O_2$ would also have been present, but the authors do not report it.

Kaufman (106) has studied the rates of several gas phase reactions of O atoms using a titration technique. He found the gas to contain 12 to 20 per cent O atoms.

Broida & Pellam (26) condensed oxygen that had passed through a microwave discharge on a surface chilled to 4.2°K. Reproducible results were difficult to obtain. No visible glow was observed to emanate from the solid which was usually a glassy white material. Upon warming, the white solid first becomes cloudy and later changes to an opaque violet color characteristic of ozone-oxygen mixtures. They suggested that the ozone might be produced by reaction of $O_2$ with O trapped in the solid and released upon warming. Bass & Broida (11) obtained absorption spectra of the condensed discharged oxygen during warm up. The ultraviolet exhibited a continuum and the visible, a large number of bands. These were observable until the temperature had risen to the point where the solid became snowy when both the ultraviolet and visible spectra disappeared and could not be brought back by rechilling. The infrared showed ozone bands. In addition one strong, unidentified band about 20 $cm.^{-1}$ wide was found with a maximum at 3496 $cm.^{-1}$. This band also disappeared irreversibly upon warming.

Broida & Lutes (24) estimated from rough calorimetric measurements that the O atom content of the solid might be about one per cent. Minkoff, Scherber & Gallagher (134) from a measure of heat release during the

warm-up of condensed, discharged $O_2$, estimate minimum O atom contents of eight per cent assuming that all the heat release comes from recombination to $O_2$, and 16 per cent assuming $O_3$ is formed. Ruehrwein & Hashman (162) and Ruehrwein *et al.* (163) made a more complete and systematic study of the production of ozone from oxygen that had been passed through a microwave discharge, condensed on a liquid helium cooled surface and then warmed. They found conversions of oxygen to ozone of as high as 78 per cent. They concluded that most of the conversion occurred in the cold trap and from the appearance of the solid decided that up to about 18 per cent conversion probably occurred on warming. These considerations lead to a maximum O atom content of the solid of about 11 per cent. However, we consider this conclusion to be very questionable. There is no evident reason, other than the appearance of the solid, to suggest that ozone is formed on warming rather than on condensing. Harvey & Bass (81) obtained infrared spectra of the solid during warm-up and were unable to find any change in the ozone content. Their accuracy limits set an upper limit of about three per cent to the O atom content of the solid. It is possible however that O atoms might either recombine or both form and destroy ozone, with little net change in ozone content; so we must conclude that these results also are inconclusive.

Wall & Brown (188) irradiated oxygen at both 77°K. and 4.2°K. with $\gamma$-rays from a $Co^{60}$ source and obtained up to 1.4 per cent ozone. No attempt was made to identify intermediates.

Jen *et al.* (103) have attempted to measure electron spin resonance of oxygen atoms in matrices of $H_2$ and A. Although in the gas phase $O(^3P_2)$ gives a line having four components (144, 146), Jen *et al.* found no resonance spectrum for O in their matrices. The authors rather tentatively concluded that the absence of a spectrum might be due to excessive line broadening, resulting from the interaction of the matrix field with orbital angular momentum of the atoms. It is, of course, possible also that no atoms were present in the matrix. It is of interest that $O_2$ trapped in argon at 4.2°K. also failed to give an electron spin resonance spectrum.

Broida & Peyron (29) showed that the $\beta$ lines observed by themselves and by Bass & Broida (10) in the condensed nitrogen afterglow were due to oxygen and attributed them to the $^1S_0 - {}^1D_2$ transition of atomic oxygen, thus indicating that atomic oxygen was trapped in the nitrogen lattice.

## The NH and $NH_2$ Radicals

The NH radical was detected by Funke (61) and by Franck & Reichardt (57) by observing the absorption at 3360 A during thermal decomposition of ammonia. Harkins (79) observed NH when an electric discharge was passed through ammonia. Ramsay (145) has made extensive studies of the spectra of NH and $NH_2$ obtained by flash photolysis of hydrazine. Flames of ammonia and oxygen and of hydrogen and nitrous oxide (63) show strong NH

and $NH_2$ emission. Pannetier (138) observed the spectra obtained on detonation of $N_3Cl$ and $NCl_3$ and reported that NH was formed if water vapor were present.

Lunt & Mills (123) observed a blue glow from a solid surface near an electric discharge in a mixture of hydrogen and nitrogen. They found a broad band at 5300–4400 A having maximum intensity at about 5000 A which they attributed to the $^1\Delta$ metastable state of NH. However, this band is in the same spectral region in which $NH_2$ is found and therefore the emission may be due to $NH_2$. More recently Rice & Freamo (150) have performed a similar experiment and concluded that the glow could not be attributed to NH. A glow with the same spectra has been found in the products from a discharge through ammonia condensed at 77°K. (11).

Robinson & McCarty have found sharp line absorption spectra of NH (159) as well as of $NH_2$ (158) in the products of a discharge through hydrazine and argon condensed at 4.2°K.

In studying the thermal decomposition of hydrazoic acid, Rice & Freamo (149) passed the vapor through a furnace at above 1000°C. and then allowed it to impinge upon a surface cooled by liquid nitrogen. A bright blue solid was deposited on the cold surface and the color persisted as long as the solid remained cold. They reported a strong paramagnetism consistent with an average of about one unpaired electron per molecule. On warming the blue color disappeared and analysis of the white solid remaining showed it to be $NH_4N_3$ and unchanged hydrazoic acid. They tentatively attributed the blue color to NH or some polymer of NH (perhaps $N_4H_4$) which reacted on warming to give ammonium azide. Subsequently, Rice & Freamo (150) found that hydrazoic acid passed through an electric discharge also gave a blue deposit at the temperature of liquid nitrogen, and they recommended this as the most convenient way of producing this material. They also found that cyanic acid treated in a similar way gave a purple deposit which turned to white upon warming. The solid above the transition point was found to consist of cyanic acid and ammonium azide. The analysis was made by mass spectrometry and, because of identity of masses, would be very difficult to distinguish from ammonium cyanate; and so the identity of the salt may be incorrect.

Rice & Grelecki (151) made material balances on the blue solid and found that no gases such as $N_2$ were evolved upon warming, the only material found on the cold surface being hydrazoic acid and ammonium azide. Franklin *et al.* (59) studied the decomposition of hydrazoic acid mass spectroscopically. They found that the products of decomposition when a Tesla discharge is passed through hydrazoic acid vapor are ammonia, hydrogen, and nitrogen. These decomposition products condensed on a surface at 77°K. gave the characteristic blue solid. Gas from the reaction zone passing directly to the mass spectrometer had essentially the same composition as that obtained upon vaporizing the blue solid collected on the cold finger down stream from the discharge. Thus the reaction is essentially complete

in the gas phase, and the ammonium azide formed on the cold surface is due largely to reactions of ammonia formed in the gas with hydrazoic acid. An attempt was made to detect NH and $N_3$ radicals and electronically excited $NH_3$ but without success. Foner & Hudson (50) found $N_2H_2$ mass spectrometrically by partially-decomposing hydrazoic acid or hydrazine in a mild electrodeless discharge, but they were unable to detect NH. The $N_2H_2$ had a much longer life than the substance responsible for the blue color and upon condensation proved to be yellow. It thus is not responsible for the blue solid observed by Rice. Mador & Williams (129) studied the blue solid from hydrazoic acid spectroscopically. They could find only ammonium azide and there was no increase in ammonium azide content upon warming. Both Mador & Williams (129) and Franklin *et al.* (59) concluded that the blue solid could contain only a very small amount, if any, of NH and $NH_2$ radicals.

Dows, Pimentel & Whittle (39) deposited hydrazoic acid from a glow discharge upon a cold surface at 77°K. They determined the infrared absorption spectrum of the solid at several temperatures during warming from 77–220°K. In addition to ammonia, hydrazoic acid, and ammonium azide, they observed some bands which they attributed to $N_2H_2$ and $(NH)_x$ in which $x$ is probably 4. Because of the fact that these bands increased upon warming at conditions where no other bands were observed to change, they concluded that the $N_2H_2$ and $(NH)_x$ must have had a precursor which they could not observe. This precursor was inferred to be NH. They were not able to estimate the amount of the unstable intermediates present. Becker *et al.* (13) photolyzed hydrazoic acid suspended in solid rare gases at 20°K. and found several infrared absorption features due to unstable molecules. They suggest that NH was trapped in xenon.

X-ray crystallographic studies of Bolz, Mauer & Peiser (18) show that the blue solid is amorphous at 77°K. Near 146°K., the color change to white is accompanied by the appearance of some crystalline structure. The lines of the x-ray diffraction pattern sharpen during the warming for about 50°C. with some accompanying heat release. There is evidence of several phases before the final end products of ammonia and ammonium azide. No direct evidence for radical trapping was found.

The paramagnetic property of the blue solid has been confirmed by the electron spin resonance absorption measurements of Gager & Rice (62). They find a large number of unpaired spins at $g = 2.003$ in blue solids made by photolysis of solid hydrazoic acid and by thermal and electrical decomposition of hydrazoic acid vapor. The absorption is a single asymmetric line about 11.5 gauss wide (36 gauss in thermally decomposed material). This has led to the tentative suggestion of F-center formation. Papazian (139, 140) has produced the blue material by a method which he has shown is a combination of electron and ion bombardment.

Although the last word has not been said about this problem, facts available at this time point rather strongly to the conclusion that the blue solid

contains very little if any NH. However, no satisfactory explanation of the blue color or its paramagnetic properties has been advanced unless one is willing to attribute it to very small concentrations of NH or its polymers, or to F-centers.

Foner *et al.* (52) have observed the electron spin resonance spectra of $NH_2$ and $ND_2$ stabilized in solid argon at 4.2°K. The radicals were prepared condensing the products of electric discharges in ammonia and by the photolysis of ammonia in argon at 4.2°K.

### The OH and $HO_2$ Radicals

The spectrum of the hydroxyl radical is found spectroscopically in electric discharges in water, $H_2-O_2$ mixtures, and other gases (21, 38, 112, 137). It has often been postulated as an intermediate in chemical reactions (113) and especially in $O_2-H_2$ and $O_2$-hydrocarbon flames, and has been detected spectroscopically in some flames (63). It has been observed mass spectrometrically by Foner & Hudson (47, 49) and by Ingold & Bryce (94) in the products of gas phase reactions of H atoms with $O_2$. Dousmanis *et al.* (38) have obtained the microwave spectra of the lambda doubling of OH and OD produced by electric discharges in water.

$HO_2$ has been postulated as an important intermediate in various gas phase chemical reactions and especially in combustion processes (113). Recently it was found with a mass spectrometer in the products of the low pressure reaction of H atoms with oxygen (47, 157) and of $H_2O_2$ with products of electric discharge dissociation of water or $H_2O_2$ (48).

When H atoms are reacted with $O_2$ and the products passed through a cold trap at 4–170°K., a glassy, usually colorless, solid is recovered (42, 64, 65, 67, 112). The amount of the deposit usually increases as the trap temperature is lowered. Upon warming, oxygen gas is evolved at about 160°K. and a solution of $H_2O_2$ in water is recovered. Similar results are obtained when water vapor is passed through an electric discharge and then condensed at low temperature (64, 69, 71 to 74, 105, 161) and when products of low pressure explosions are condensed at low temperatures (43, 45). Various intermediates have been proposed to account for the formation of $H_2O_2$ and for the evolved oxygen, including an isomeric form of hydrogen peroxide, $H_2O$—O(57), various radicals including OH (161) and $HO_2$ (71, 72), and super oxides such as $H_2O_3$ and $H_2O_4$ (69). None of these explanations has proved completely satisfactory. Recently Hogg & Spice (91) and Edwards & Hashman (42) from careful studies of the reaction products and observations of the solid concluded that the "evolved" oxygen had been held at low temperatures in a gel-like structure of water and hydrogen peroxide. Although this problem is probably not finally solved we are inclined to accept this latter explanation as the most probable one.

Robinson & McCarty (159) decomposed hydrazine containing water vapor in an electric discharge and condensed the product gases immediately at 4.2°K. They obtained the ultraviolet spectrum of the solid and found a

band at 32090 cm.$^{-1}$ which they identified as the 0, 0 band of OH, shifted 300 cm.$^{-1}$ by the matrix. Bass & Broida (11) obtained absorption spectra between 0.31 and 3.5 $\mu$ of discharged water condensed at 4 and at 77°K. Some weak unidentified absorption was found, and, in particular, a sharp absorption band at 4151.5 cm.$^{-1}$ which requires both the low temperature and the discharge for its appearance.

Livingston *et al.* (118) passed water vapor through a discharge, deposited it on a liquid nitrogen cooled surface, and obtained the paramagnetic resonance spectrum. They found a peak at $g = 2.0085$, having a shoulder at 2.027. They consider that this might arise from a randomly oriented species having an anisotropic g value. Either OH or $HO_2$ might exhibit this behavior, but it is not certain that either is responsible. They estimated that, if the radical was $HO_2$, it was present in about 0.3 per cent concentration; if OH, the concentration was about 0.15 per cent. Neither would be sufficient to account for the $H_2O_2$ produced or the $O_2$ "evolved" upon warming. Matheson & Smaller (130) and Smaller *et al.* (173) obtained paramagnetic resonance spectra of $H_2O$ and $D_2O$ ice irradiated with $\gamma$-rays at 77°K. and observed, in addition to lines they thought due to free H or D, a closely spaced doublet or triplet which they attributed to OH or OD, respectively. These spectra do not agree with those of Livingston *et al.* (118) discussed above, and both can not reasonably be attributed as OH or $HO_2$ radicals. Glassy solutions of $H_2O_2$ in water when irradiated at 77°K. with the 2537 A line of mercury give a single broad line which might be OH or $HO_2$ (70, 96).

### Various Organic Radicals

A large number of organic radicals have been "identified" from electron spin resonance spectra obtained on various organic solids that have been subjected to ultraviolet, gamma-, or x-radiation at low temperatures. From the spectrum, a radical of appropriate structure and composition is selected upon the basis that the number of lines is one greater than the number of equivalent protons. Even quite complex molecules in these considerations usually turn out to produce only a single radical, although several might reasonably be expected. In only a few cases have methods other than electron spin resonance been employed to identify the radicals. A recent book by Ingram (95) discusses and summarizes the applications of electron spin resonance techniques to free radical investigations.

Probably the only energetic organic radical that has been identified with reasonable certainty is methyl. Gordy & McCormick (77) found a quartet in the electron spin resonance spectrum of zinc dimethyl irradiated with x-rays at 77°K. and attributed this to methyl. Smaller & Matheson (172) and Wall *et al.* (189) irradiated solid methane at 4°K. with $\gamma$-rays and also found a quartet with intensities of approximately 1:3:3:1 in the electron spin resonance spectrum. Wall *et al.* (190) also find the typical H atom doublet and noted that upon warming the H atoms disappeared more rapidly than the methyl radicals. They estimated the total radical content of the

matrix to be 0.08 per cent. Jen *et al.* (103) passed methane through a mild electric discharge and trapped the products at 4.2°K. They also irradiated methyl iodide with ultraviolet light at this temperature. In both cases they found the typical quartet spectrum which they attributed to methyl. Mador (128) photolyzed $CH_3I$ and $Pb(CH_3)_4$ at 4.2°K. and obtained a red solid that decomposed violently upon warming. He attributed this behavior tentatively to $CH_3$ but was unable to detect the expected infrared vibrational bands, probably because the radical concentration was very small.

The spectrum of $Hg(C_2H_5)_2$ irradiated at 77°K. obtained by Gordy & McCormick (77) was a symmetrical sextet which they attributed to ethyl radical. Smaller & Matheson (172) found a quartet of triplets in irradiated ethane which they also attribute to ethyl and conclude that matrix broadening in Gordy & McCormick's spectrum made it impossible for them to resolve the spectrum completely. Irradiation of ethylene and ethyl chloride gave spectra identical to that of irradiated ethane and this, according to Smaller & Matheson, supports the conclusion that the ethyl radical is responsible. It is not clear why methyl, methylene, and vinyl radicals might not also be produced and contribute to the spectrum. The authors, however, prefer to consider that the spectrum is of ethyl, which leads to the conclusion that the five hydrogens couple equally although they are not equivalent chemically. Chestnut (31) has treated hyperfine interactions in aliphatic free radicals by the molecular orbital method and concludes that this is possible. Luebbe & Willard (122a) find ethyl radicals by electron spin resonance in glassy ethyl iodide irradiated with $\gamma$-rays at 70°K. and about one per cent as many H atoms; the polycrystalline solid indicated an ethyl radical content about thirty to fortyfold less than the glassy solid.

Smaller & Matheson (172) have obtained electron spin resonance spectra of several other hydrocarbons irradiated at 77°K. and have interpreted the results in terms of various single radicals. These include propane, *n*-butane, cyclohexane, cyclopentane, propylene, and several hydrocarbons of higher molecular weight. Luck & Gordy (122) have irradiated several light alcohols, amides, ammines, and mercaptanes with x-rays at 77°K. Gibson *et al.* (70) and Fujimoto & Ingram (60) have irradiated several alcohols in water—$H_2O_2$ glass with 2537 A mercury radiation at 77°K. All experimenters found a triplet with methanol. Luck & Gordy found a triplet with irradiated $CH_3ONa$ also. Luck & Gordy attributed the triplet in both instances to $CH_2^+$ on the basis that decomposition of $CH_3OH^+$ to $CH_2^+$ and water would be favored energetically. This is contrary to known energetics of ion formation from methanol as determined by electron impact methods (46). Further, the existence of these ions in sufficient quantity for reliable electron spin resonance measurements would require that electrons be unable to diffuse through the solid under conditions where H atoms and even methyl radicals disappear rather rapidly, and so we consider this interpretation erroneous. Gibson *et al.* (70) attributed the triplet that they observed to $CH_2OH$, and

we are inclined to consider this or similar radicals as the more reasonable interpretation of Luck & Gordy's results also.

Quintets were obtained in the spectra of irradiated ethanol and propionamide (122), $Hg(CH_3)_2$ (77) and of alanine (76). These were attributed to $C_2H_4^+$. In our opinion a more reasonable source of these spectra, if a single species is indeed involved, would be a radical $CH_3$—CH—R where R, if it contains protons, has them sufficiently removed from the electron that interaction is negligible. This conclusion is also supported by Symons & Townsend (177) who found that ethanol irradiated with ultraviolet light at 77°K. in a rigid glass was paramagnetic and purple in color with a broad spectral band at 517 mμ. Color and paramagnetism disappeared on warming. The authors attributed this behavior to $CH_3CHOH$.

Various experimenters subjected other organic materials to irradiation at low temperatures and measured the electron spin resonance of the products. No attempt will be made to discuss these in detail but a few will be listed. Compounds studied in this include ethyl iodide (96, 122a), benzyl alcohol and benzyl amine (96), various alcohols and acetone (4, 6, 7), several hydrocarbons, alcohols, aldehydes, ketones, acids, esters, ethers, halides, and nitro compounds (5), various amino acids (76), and several polymers (1, 2, 3, 8, 9, 97, 166, 167).

Norman & Porter (135, 136) irradiated toluene and various benzyl derivatives in "glasses" at 77°K. with ultraviolet light and detected the benzyl and other radicals spectroscopically. Papazian (139) suggests that the color changes produced in solid $CH_3I$, $CH_3OH$, and $(CH_3)_2NH$ by a Tesla coil discharge may be caused by trapped radicals.

### Others

Robinson & McCarthy have detected HNO (159) and $NO_2$ (160) by infrared absorption spectroscopy in an argon matrix at 4.2°K. Jen *et al.* (103) also obtained an electron spin resonance spectrum for $NO_2$ in an argon matrix at 4.2°K. but were unable to obtain a spectrum for Cl or NO. NO and possibly $NO_2$ have been detected by their emission spectra in the solid nitrogen glow (10, 29). Norman & Porter (135, 136) irradiated various organic iodides in rigid glasses and demonstrated the presence of iodine atoms by the development of color on warming the glass. They also detected CS and ClO spectroscopically after irradiation of $CS_2$ and $ClO_2$ in a glass. Rice & Scherber (155) decomposed hydrazine and obtained a yellow deposit at 77°K. The solid was not paramagnetic and was attributed by the authors to tetrazane. In view of the recent results of Foner & Hudson (50) it seems more probable that the color was due to $N_2H_2$. Rice & Grelecki have decomposed $(C_2H_5)_2NH$, $CH_3N_3$ and $(CH_3)_2N_4(CH_3)_2$ (152), $CH_3N_3$ (154), and $(CH_3)_2NH$ (153) in the gas phase and deposited the products upon a cold surface. The colors of the resulting solid were attributed to various postulated free radicals or their polymers. Rice (147) also reports colored de-

posits resulting from sudden freezing of the decomposition products of dimethyl disulfide and di-butyl disulfide and attributed the color to methyl sulfide and *t*-butyl sulfide radicals. Rice & co-workers deposited purple (156) and green (148) forms of sulfur by condensing sulfur gas at 500–700°C. and 0.1 to 1.0 mm. pressure on a liquid-nitrogen cooled surface. Edwards & Hashman (41) have deposited magnesium from the gas in a very dilute argon matrix. The solid was red and turned black irreversibly upon warming. The red color is probably due to atomic nonmetallic magnesium. Similar results were obtained with sodium (12). Sowden & Davidson (174) have photolyzed several solutes in rigid hydrocarbon glasses at 77°K. and found many complex effects after ultraviolet irradiation and subsequent warm-up. However they did not succeed in definitely identifying trapped reactive species.

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# PHYSICAL ORGANIC CHEMISTRY[1]

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Physical organic chemistry is a broad division of chemistry which cuts across the subject both in its methods and in its objectives. The current rate of publication in the field, as estimated from the list of titles printed in *Current Chemical Papers*, certainly exceeds 100 per month; the exact figure will depend on the personal point of view of a reviewer. In the survey of such an enormous volume of publications one is obliged to adopt a rather ruthless method of selection, and it is altogether impossible to avoid some subjective bias. In making his selection of material for this article, the writer was guided by the view that the distinctive purpose of an "annual" review could best be served by giving a rather general survey of a number of topics on which research seemed to have been particularly intensive and fruitful during 1958, but he has also borne in mind that exceptionally up-to-date and informed reviews on certain selected subjects were contributed to Volume 9 or are available elsewhere. These have been omitted or given less prominence.

The subject matter included agrees quite well with the systematic definitions, on an operational basis, of physical organic chemistry, as given by Taft, Deno & Skell in last year's review (1). However, the writer hopes that the material chosen by himself and by his predecessors in this series will not contribute to perpetuating too rigid a definition. It is the aim and *raison d'être* of a borderline subject, such as physical organic chemistry, to include those territories of science which are shut out by the established demarcation lines of conventional subjects. Any rules which seek to delimit its scope as a distinctive discipline could ultimately reproduce that compartmentalization which the pioneers in the field set out to break down.

Recent reviews in Western languages of topics not specifically mentioned in this article concern mechanisms for C—H bond breakage (2); nucleophilic aromatic substitution (3) and, more specifically, benzyne intermediates in them (4, 5) and cine-substitutions (6); neighbouring-group effects (7); thermochromic, piezochromic, photochromic, and photomagnetic phenomena (8); oxidation by permanganate (9); by chromium and manganese compounds (9a), ferricyanide (10), and lead tetra-acetate (11); certain classes of organic peroxides and their relation to autoxidation (12), free-readical reactions in solution (13) and their stereochemistry (14), and the detection of free radicals by electron spin resonance (15, 16); free valence in conjugated organic molecules (17); the stereochemistry of displacements at unsaturated centres (18) and of optically labile compounds (19); steric effects on mesomerism (20); and solvolyses of phosphate esters (21, 22).

[1] The review of the literature was concluded November 20, 1958.

## Structure

*Rotational barriers.*—The old problem of the origin of the potential barrier to rotation about single bonds in molecules such as ethane has been reconsidered. Pauling (23) has pointed out that potential barriers arise from the interaction of adjacent hybrid bonds with a small amount of *d* and *f* character and has shown that this effect might well be of the right order of magnitude to give a complete explanation of the phenomenon. He has used this theory to predict rotational barriers in different structures. Eyring, Stewart & Smith (24) express the belief that a staggered conformation in ethane is preferred because with it the electron path in the delocalized H—C—C—H orbitals will be "smoothest."

New experimental investigations of the rotational isomerism, barrier heights, and rates of isomerization have used nuclear magnetic resonance spectroscopy (25, 26) and ultrasonic relaxation effects (27, 28).

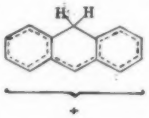
The importance of rotational barriers and preferred conformations in acyclic systems is receiving increasing recognition in the quantitative consideration of reaction mechanisms (29 to 32).

An interesting related problems is the relative rotation of the two rings in substituted ferrocene. Existing evidence is entirely in favour of free rotation (33), but it would not rule out a low barrier.

Conformational equilibrium constants in alicyclic systems have been obtained from spectroscopic and kinetic observations (34 to 39). The application of nuclear magnetic resonance spectroscopy is confirming and extending the principles of conformational analysis in cyclic structures (40 to 43). Conclusions drawn from chemical considerations of conformational analysis have been critically examined in some detail (44, 45).

In this connection the full report of Bottini & Roberts's study of nitrogen inversion of N-substituted imines also should be mentioned. For the substituted ethylene imines they were able to deduce the rates of inversion from the temperature dependence of nuclear magnetic resonance spectra, but it was found that imines with four-, five-, and six-membered rings inverted too rapidly for observation (46).

*Organic ions.*—Some important results concerning the structure of carbonium ions have been reported since the publication of a recent review of that subject (47). The structure 1




1.

proposed for the conjugate acid of anthracene (48) has found support from substituent effects on absorption spectra (49, 50 and unpublished observations quoted in Ref. 2) and has now been elegantly confirmed by the detec-

tion of $CH_2$ groups in the nuclear magnetic resonance spectra of some aromatic hydrocarbons in acidic solvents (51). These structures have also continued to form the basis for the interpretation of aromatic hydrocarbon basicities. An extensive coherent set of basicity measurements in $HF—BF_3$ has been published during the year (52, 53).

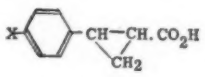
A considerable volume of publications deals with the detection by electron spin resonance, of positive and negative radical ions formed from aromatic hydrocarbons by loss or gain of an electron under oxidizing or reducing conditions, and with the interpretation of the resulting electron spin resonance and optical spectra (54 to 58, and references cited therein). The monopositive paramagnetic ions can be formed by the action of sulphuric acid, as are the diamagnetic protonated cations of structures analogous to 1. More work is required to establish the exact conditions under which each of the two kinds of ions is formed and the rates and mechanisms of their interconversions. The reactions appear to be reversible and dependent on hydrocarbon structure and the oxidizing power of the media (50).

The more general application of nuclear magnetic resonance spectra for the purpose of establishing the position of protonation of bases and the nature of analogous equilibria seems promising. The method has been used to show that in strongly acidic solutions of amides the proton is attached to the oxygen atom (59).

Interest in symmetrical organic ions with odd-membered rings continues. Experimental evidence for the equivalence of the carbon atoms of the tropylium ion has been presented (60) and other publications deal with a calculation of the resonance energy of the *s*-triphenylcyclopropenyl cation (61) and with the experimental detection of substituted cyclopropenyl anions (62).

An organic cation containing boron has been reported (63).

*Conjugation in cyclopropane systems.*—The effect of different *p*-substituents on the dissociation constants for acids of the structure 2




2.

has been examined. The results have been fitted into the $\rho\sigma$-analysis and the $\rho$-value for the series is found to be 0.182. This is slightly smaller than the value for the corresponding series of $\beta$-arylpropionic acids ($\rho = 0.21$) and considerably smaller than that for the cinnamic acids ($\rho = 0.466$). The conclusion drawn is that the electronic transmission through the cyclopropane ring is inductive, as in the arylpropionic acids, and not conjugative. It is suggested that spectral observations which indicate the occurrence of conjugation could be reconciled with the above result if it were assumed that the cyclopropane ring transmits conjugation in the excited state but not in the ground state (64).

## Equilibria and Reactions

*Ionic association.*—There is a steadily increasing awareness of the importance of ion pairs and larger ionic clusters in controlling the kinetics and product composition of organic reactions. It is interesting to be reminded (65) that different chemical behaviour of free and associated phenoxide ions was postulated by Ingold in 1926 (66) and that the suggestions made then satisfactorily explain new work on the position of alkylation of alkali-metal salts of phenols by benzyl and allyl halides. *O*-Alkylation is increased, relative to nuclear alkylation, by conditions in which dissociation is favoured (65).

Winstein and his collaborators have continued to interpret with success their kinetic results on the solvolysis of substituted $\beta$-phenylethyl systems, mainly in acetic acid, in terms of the existence of experimentally distinct "intimate" and "solvent-separated" ion pairs (67, and earlier papers of the series). They have shown that this model has a sufficient number of degrees of freedom to give a satisfactorily detailed account of the observed experimental complexities. The results now describe with some precision the factors governing the equilibrium between the two types of ion pair. The analysis is ingenious and, if the model has physical reality, it should be possible to discover its experimental manifestations apart from the group of kinetic results which caused its postulation. Experiments with this objective are eagerly awaited.

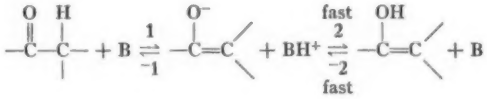
In benzene solutions, nucleophilic substitution reactions of triphenylmethyl chloride have been interpreted by Hughes and Ingold in terms of mechanisms which involve clusters larger than ion pairs, a specific postulate being the assumption that different arrangements of ions within a cluster are distinguishable (68). The occurrence of ionic aggregates in benzene, although not as yet the specific proposals concerning their structure, are well supported by other physical data (conductivity measurements) (69). Swain & Pegues have criticized the detailed formulation of the mechanism (70) and prefer to interpret the kinetics of these reactions in terms of Winstein's postulate of different kinds of ion pairs (67). The system is a difficult one both theoretically and experimentally, and some discrepancies between the experimental results of the two laboratories remain to be resolved.

Recent work by Pocker (71) suggests that ionic association does not occur in nitromethane solutions at ionic strengths of the order of 0.001 *M*. His results imply that the ionization of triarylmethyl chlorides in nitromethane is not as simple an equilibrium as hitherto assumed. They throw considerable doubt on the interpretation of the extensive series of ionization constants of triarylmethyl chlorides in nitro-alkanes which were held to indicate the formation of undissociated ion pairs (72, and earlier papers by Evans *et al.*).

*Kinetic isotope effects.*—The effect on reaction velocities of the replacement of $^1H$ by $^2H$ or $^3H$ in a chemical system has been widely used as a mech-

anistic criterion, and great progress has been made since the subject was reviewed in 1955 (73, 74).

The familiar and simple use of deuterium oxide in place of water for the detection of rapid proton-transfer pre-equilibria in acid-base catalyzed reactions has again come into favour (75 to 78). The subject has benefited from a thorough experimental study and thoughtful discussion of the base-catalyzed keto-enol transformations of methylacetylacetone by Long & Watson (79). In the enolization reaction, which is known to follow the mechanism



it was possible to study separately the effects of solvent change and of deuterium substitution at the $\alpha$-position, under the influence of either water or acetate ion as the catalyzing base. By a combination of these measurements with the equilibrium constant, the corresponding effects for the proton transfer reaction $-1$, involving $H_3O^+$ or acetic acid in the role of the acid $BH^+$, were derived. The analysis explains satisfactorily why the isotopic solvent change has a much larger effect on slow proton transfers from weak acids than from the solvated hydrogen ion. It confirms the usual assumption that reactions catalyzed by strong acids will go more slowly in $D_2O$ if there is a slow proton transfer to the substrate and slightly faster if there is a protonation pre-equilibrium. For the uncatalyzed hydrolysis of methyl halides and methyl esters this solvent effect is rather small (80).

Several investigations have again used the relative rates of substitution at —C—$^1$H and —C—$^2$H bonds to decide whether C—H bond breaking makes progress in the formation of the transition states (81 to 88).

The observation has been made that the iodination and diazo-coupling of imidazole occur at different positions, although both reactions are apparently electrophilic and occur by substitution in the conjugate base of imidazole. It is also found that the isotope effects of the two reactions are totally different, being large in the case of iodination and absent from coupling. It has been suggested therefore that the orientational change occurs because the proton loss is partly rate-determining in iodination (89). The hypothesis is attractive and ought to be tested for any other electrophilic substitution reactions in which the position of attack depends on the reagent.

Trends in the values of $k_H/k_D$ ratios have been noted for several series of aromatic side-chain halogenations. The ratios run parallel with activation energies (85)—as has also been observed for certain carbon-isotope effects (90)—but it is not yet possible to interpret the exact values of $k_H/k_D$ in any detail.

Shiner has suggested that the slightly larger isotope effect associated with Hofmann eliminations of the kind

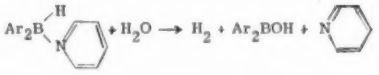
$$CD_3 \cdot CH_2 \cdot \overset{+}{N}Me_3 + B \rightarrow CD_2{:}CH_2 + NMe_3 + BD^+$$

implies a larger anion character for the transition state than in the case of the E2 reaction

$$CH_3 \cdot CDPh \cdot CH_2Br + B \rightarrow CH_3 \cdot CPh{:}CH_2 + BD^+ + Br^-$$

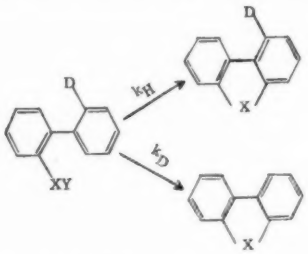
The absence of deuterium exchange with the solvent at the $\beta$-position of the ammonium compound under the reaction conditions shows that the mechanism does not involve the conjugate base (mechanism Elcb) (91). These conclusions have been largely confirmed with tritium-labelled ammonium bases, but the existence of an anomalous intramolecular isotope effect has also been inferred from these measurements (92).

For the reaction



in acetonitrile as a solvent, it has been shown that deuterium replacement in the B—H link has a much smaller effect on the rate ($k_{BH}/k_{BD} \sim 1.5$) than the replacement of $H_2O$ by $D_2O$ ($k_{H_2O}/k_{D_2O} \sim 7$) (93). The small value of the first ratio may be characteristic of hydride transfer reactions.

A family of reactions which lends itself particularly well to the study of isotope effects in aromatic substitutions are the cyclizations




where the ratio $k_H/k_D$ is obtained from the proportion of deuterium in the product. When $-XY = -CHO, —CO_2$ (from the decomposition of the diacylperoxide) and $—CH{=}N{=}N$, the respective products are fluorenone (cyclization in the presence of di-*tert*-butyl peroxide), the lactone of 2-carboxy-2′-hydroxybiphenyl, and fluorene, the corresponding $k_H/k_D$ ratios being 1.38, 1.32, and 1.12 (94). The cyclization of *o*-phenylbenzoic acid ($—XY = -CO_2H$) to fluorenone in acid solutions leads to $k_H/k_D$ values in the range 1.13 to 3.02, depending on the acid used. When it is borne in mind that

aromatic deuterium exchange is expected to be very rapid with the acidities used in this investigation, it does not seem certain that these results were unaffected by exchange reactions, although a control experiment is cited (95).

The effect of deuterium substitution on reactions involving adjacent bonds is generally small and comparative rate measurements are perhaps as yet insufficiently precise to test fairly the theoretical explanations that have been put forward over the last few years and mentioned by Streitwieser *et al.* (96). A list of $\alpha$-deuterium effects observed in nucleophilic substitution reactions (97) contains seven determinations covering the range 0.94 to 1.17 for the ratio $k_H/k_D$. Expressed as a contribution to the free energy of activation per $\alpha$-deuterium atom, the effects extend from $-15$ to 97 cal. Of similar magnitude are $\beta$-Deuterium effects. A recent theory (96) based on Bigeleisen's treatment of kinetic isotope effects, ascribes the $\beta$-effect to a bending mode of the C—H bond in the direction of the molecular orbital formed from C—H hyperconjugation with the vacant $p$-orbital at the seat of substitution. The $\alpha$-effect is attributed to a wagging mode and may give a measure of solvent participation in $S_N1$ substitutions, according to these authors. It has been suggested (98) that an $\alpha$-deuterium effect is found in $S_N1$ reactions but not in $S_N2$ reactions, or (97) that the effect of $\alpha$-deuterium on the rate is roughly related to the proximity of outgoing and incoming groups to the $\alpha$-hydrogen atom and the sequence of $k_H/k_D$ values is approximately the same as the order of "increasing necessity of nucleophilic attack from the rear." This is reconcilable with the previous theory (96) if the force constant of the relevant C—H mode in the transition state is sensitive to the proximity of these groups.

$\alpha$- and $\beta$-effects have been measured for the formolysis and acetolysis of $Ph\cdot CH_2\cdot CH_2\cdot OTs$ ($Ts = p-MeC_6H_4SO_2$) and related to the extent of rearrangement (thought to be a measure of phenyl participation) that accompanies the reaction (99). For the $S_N1$ solvolysis of $Me_2CH\cdot CH(Me)\cdot OTs$, the replacement of the $\beta$—H atom by deuterium causes a larger reduction in rate ($k_H/k_D \sim 2.2$). In the main products of this reaction the $\beta$ C—H bond is severed, and the large isotope effect on the rate implies that it has become appreciably loosened in the transition state (100).

An inductive effect of the C—D bonds (relative to C—H), proposed by Halevi (101), may play some role in the full explanation of these phenomena. The reality of this effect is suggested by the influence of deuterium substitution on the fluorine nuclear magnetic resonance spectra of heptafluoropropane. The shift of the fluorine resonance indicates that C—D is more electron-donating than C—H (102). Deuterium or tritium substitution in the side-chain of toluene exerts no detectable effects on nuclear nitration or mercuration, but a small retarding effect seems to have been established for bromination (103).

The promising results obtained with $\alpha$- and $\beta$-deuterium effects are sure to stimulate more extensive measurements in the near future. In view of the smallness of the effects, the rate comparisons require considerable precision.

It seems that perhaps insufficient attention has been paid so far to the problem of purifying the isotopic materials to the same extent as the usually more abundant unlabelled reagents. A subtle source of error lies in the fact that the labelled and unlabelled materials are often prepared by different synthetic routes and are liable to contain different contaminants. It is therefore recommended that the adequacy of the purification of the labelled materials should always be checked by preparing and purifying a control specimen of unlabelled materials from the same starting material by exactly the same route and on the same scale. The degree of concordance between rate constants obtained with purified ordinary material (resulting from a large-scale preparation and careful purification) and the unlabelled control specimen should help to establish the limits of error from this source.

Isotope effects involving the carbon isotopes are usually even smaller than $\alpha$- and $\beta$-hydrogen effects (104, 105), and an attempt to apply the $\alpha$-carbon isotope effect to the diagnosis of $S_N1$—$S_N2$ reaction mechanisms led to inconclusive results (106). Carbon- and oxygen-isotope effects can clarify, however, which bonds are broken in the slow step of a complex reaction mechanism (107, 108).

*Reactions of unusual speeds.*—The application of nuclear magnetic resonance spectroscopy to the study of rapid intramolecular changes has been mentioned earlier. Further progress has been made with this technique in following the rates of proton-transfer processes (109, 110).

The exceedingly slow decarboxylation of alanine, the runs having half-lives greater than $10^4$ years, has been followed by a low-level counting technique applied to the carbon dioxide evolved (111).

*Acidity functions.*—New measurements of the $H_0$ function have been carried out for aqueous solutions of several weak acids (112); for solutions of perchloric acid (up to 0.3 *M*) in acetic acid-water mixtures (113); for boron trifluoride in phosphoric acid (114); on certain solutions of propene and hydrogen chloride in phosphoric acid (115); and for solutions in acetic acid of hydrogen chloride (116), of zinc chloride and hydrogen chloride (117), and of stannic chloride (118).

$H_0$ measurements for the solvent system ethanol (20 per cent)—$H_2SO_4$—$H_2O$ and $pK$ values for a series of substituted azobenzenes have also been reported (119). An interesting suggestion (based on a $\rho\sigma$ analysis of the data) arising out of the work is the hypothesis that the proton is symmetrically attached to the two nitrogen atoms of the azo group.

4:4′-Dimethoxydiphenylmethyl acetate has been used as indicator in the solvent systems acetic acid-sulphuric acid (83) and acetic acid-zinc chloride-hydrogen chloride (117). The ionization produces carbonium ions and the measurements can be considered to apply to an acidity function which is related to, although not identical with, the function $J_0$ (83).

Indicator measurements have been carried out by Kwart and Weisfeld for acid solutions in ethanol-water where the $H_0$ function does not exist. However, they suggest that a combination of their measurements with

Grunwald's theory of solvent effects leads to a usable criterion for the experimental distinction between A-1 and A-2 reactions (120). The suggestion is of considerable interest and a more thorough test of its predictions is awaited.

It has been proposed that the gradual loss of the fine structure in the ultraviolet spectra of benzene and methylbenzenes in acidic solutions can be used to establish an acidity scale based on electron mobility. It is stated that the function would be related to but not identical with $H_0$ (121). It is not altogether clear how much generality a function of this kind could be expected to possess. In highly acidic media, mesitylene and hexamethylbenzene are said to behave in the manner of Brønsted bases and to be suitable for use as $H_0$ indicators (121).

Numerous kinetic applications of the $H_0$ function for the purpose of establishing reaction mechanisms have been made again. Typical examples which have been added to the list of reactions reported as following $H_0$ are the hydrolysis of $\beta$-isovalerolactone (122), the dehydration of $p\text{-}CH_3O\cdot C_6H_4\cdot CH(OH)\cdot CH\cdot CH_2\cdot CO\cdot CH_3$ (123), the pinacol rearrangement and the simultaneous oxygen-isotope exchange (124), the Prins condensation of olefins and formaldehyde (125), and the decomposition of cumene hydroperoxide (126). The last case relates to a medium containing ethanol and water in equal amounts, perchloric acid, and lithium perchlorate; and it is rather doubtful that the acidity-function principle is valid. The decomposition of chloroform in methanol-sodium methoxide closely parallels indicator measurements of 2:4-dinitroaniline which are taken to define the $H_-$ function in this system (127).

The relationship between dissociation constants and solubilities of aromatic sulphonic acids and the functions $H_0$ and $H_-$ of aqueous sulphuric acid has been discussed (128).

For the decarbonylation of 2:4:6-tri-isopropylbenzaldehyde in sulphuric acid, Schubert and Myhre find the rate to pass through a maximum at ~80 per cent sulphuric acid (129). This kind of behaviour has been observed by Schubert and his collaborators for several aromatic decarbonylations and decarboxylations. It is interpreted by ascribing to the acid media the dual role of catalyzing the decomposition and converting the substrate by protonation into an unreactive species. Such a mechanism requires a complex dependence of rate on $H_0$.

The mechanism of the hydration of olefins in strong aqueous acids (130) and the dehydration of arylmethylcarbinols (131) has been further discussed. In the latter case a complication (the formation of an intermediate ether) has been found to intervene under certain conditions. The proper understanding of these particular reactions and the significance of their acidity-dependence is at present a key problem in the interpretation of the Zucker-Hammett hypothesis (1).

*Reaction at high pressures.*—The effect of high pressures has been studied for the nucleophilic aromatic substitution reaction between bromoquinolines and bromonaphthalene (132). The influence of pressure has also been ex-

amined in relation to conformational effects (133) and in relation to $S_N1$ and $S_N2$ mechanisms and borderline cases (134).

This may also be the place to mention that intriguing observations have been made on the cleavage of aromatic and heterocyclic rings, in compounds such as bromobenzene and pyrrole, under the influence of ultrasonics (135).

*Friedel-Crafts reaction.*—The nuclear alkylation and acylation of aromatic compounds under the influence of a metal halide catalyst has remained one of the most widely used and studied reactions and one whose mechanism is least well understood. Its investigation by the methods of reaction kinetics is beset with a number of practical and theoretical difficulties. Dryness of reagents and purity of the metal halides are essential practical requirements in view of the known occurrence of co-catalysis by water and hydrogen halides. In the reviewer's opinion, most of the theoretical difficulties arise out of the use of solvents of low dielectric constant and unknown or imperfectly-known electrochemical solvent behavior. In a solvent such as benzene, even a seemingly simple reaction between two reagents, such as the halide exchange of triphenylmethyl chloride, assumes complex features which are thought to arise from equilibria between ionic aggregates of different structure (68, 70). The Friedel-Crafts reaction requires as a minimum three different reagents, and the number of possible combinations for complex and cluster formation is vastly greater.

Brown *et al.* have recently reported kinetic investigations in which nitrobenzene was employed as the solvent (136 to 139). The complexing of aluminum chloride by nitrobenzene and benzoyl chloride, as well as the formation of colored ternary complexes between solvent, aromatic compound, and aluminum chloride, are indicated. Benzoylation and benzenesulphonylation velocities in this system are of first order with respect to acid chloride but exhibit no recognizable order with respect to aluminum chloride. The order with respect to aromatic compound in benzenesulphonylation is stated to be zero for reactive compounds, typified by xylene, and unity for unreactive compounds, such as benzene. The authors suggest that this situation may be similar to that in aromatic nitration, requiring in some cases a rate-determining process not involving the aromatic compound. Some of the results can be rationalized in this manner, but it is difficult to avoid the conclusion that a unique explanation of the findings is impossible at our present stage of knowledge concerning solutions in nitrobenzene.

The exploratory study of a simpler system has been reported by Brown & Jensen in another group of papers (140 to 144). In these experiments the acid chloride itself served as the solvent, and the kinetic order with respect to the acylating agent was thus eliminated. It also follows that the kinetic order yields no information concerning complexes formed by the acylating agent. The experiments permitted reactivity comparisons of different aromatic substrates, as well as of different metal-chloride catalysts. Most of these results support the authors' views concerning the connection between reac-

tivity and selectivity, although some apparent contradictions are noted. For benzenesulphonylation the catalysts are found to follow the sequence of reactivity $SbCl_5$, 1300; $FeCl_3$, 570; $GaCl_3$, 500; $AlCl_3$, 1; $SnCl_4$, 1/350; $BCl_3$, 1/1600; and $SbCl_3$, very small (142). The order is noteworthy in that, contrary to usual experience, aluminum chloride is not the most efficient catalyst. This type system appears to be more promising than the use of an inert solvent, and it should be possible to study the equilibria involving the catalyst by physical measurements independently of the kinetics.

A simpler model system for Friedel-Crafts alkylation was examined by Bethell & Gold who studied the rate of formation of triarylmethanes in acetic acid solution from benzhydryl acetate and an aromatic compound, under the influence of sulphuric acid (83) or zinc chloride-hydrogen chloride (145) as the catalyst. In the case of zinc chloride, the only complex formation observed is between it and hydrogen chloride and with acetic acid, and the sole function of the catalyst is found to be the promotion of the ionization of the aralkylating agent to carbonium ions. Catalytic activity is directly related to the Brønsted acidity [as measured by indicators (117) or by the velocity of aromatic hydrogen isotope exchange (146) induced in the medium]. The experimental conditions of these experiments are even further removed from those applying to the usual Friedel-Crafts procedure, and the conclusions are not necessarily valid in the changed circumstances. However, the general implication of this investigation, viz., that proton activity in the medium plays a part in determining catalytic activity, seems to be supported by the finding that the alkylation of benzene (as solvent) by alkyl benzenesulphonates is catalyzed by acid (147). Acid catalysis of alkylations by alkyl chlorides again is not unreasonable in view of the distinct basicity of the chloride ion in benzene solution [which manifests itself, for example, in the formation of the triple ion $HCl_2^-$ on addition of hydrogen chloride (69)] and is a possibility that ought not to be categorically discounted.

The addition compounds formed between Friedel-Crafts catalysts and organic molecules have been studied from the structural point of view. The infrared spectra of the complexes between catalysts of the Lewis acid type and a variety of organic compounds have been reported (148 to 152). These confirm with some certainty an attachment between the catalyst and a particular functional group in the molecule (hydroxyl, carbonyl, nitrile, olefinic double bond, ether oxygen, or tertiary nitrogen) (148). The data on aromatic ketones and a series of catalysts (boron trifluoride, ferric chloride, zinc chloride, and aluminum chloride) suggest a parallelism between the usual order of catalytic activity and the shift of the carbonyl vibration frequency (152). Measurements of the dipole moments of complexes between stannic chloride and organic acids (153) and between nitrocompounds and aluminum bromide have been carried out (154).

The electrochemical study of stannic chloride as a solvent system indicates that cyclohexanone functions in it as a base (155).

Other relevant aspects of the subject covered in recent papers are the role of $Ph_3C \cdot SnCl_5$ in the catalysis of styrene polymerization by stannic chloride

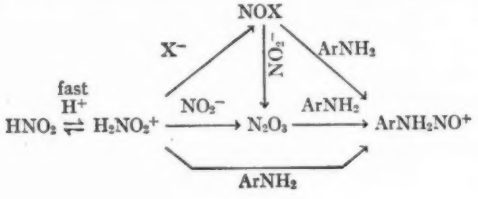
(156), rearrangements of branched alkylbenzenes (157), a comparison of the case of interchange of $\alpha$- and $\beta$-carbon atoms in the side chain of a *n*-alkylbenzenes under the influence of aluminum chloride (158) and related work on the alkylation of benzene with $^{14}$-labelled ethyl chloride (159), the isomerization of [$\beta$—$^{14}$C] ethylcyclohexane (160), and the reaction of phenol with diols in the presence of phosphoric acid (161), and the isopropylation of benzene under the influence of tertiary bases and aluminum chloride (162).

*Reactions of nitrous acid.*—Hughes, Ingold, & Ridd have fully reported kinetic studies of aromatic diazotization in weakly-acidic aqueous solutions (163 to 168). The results are consistent with the view that the rate of diazotization is controlled by N-nitrozation, the detailed steps of the reaction being

$$ArNH_2 \xrightarrow{slow} Ar\cdot NH_2NO^+ \xrightarrow{fast} ArNH\cdot NO \xrightarrow{fast} Ar\cdot N{:}N\cdot OH \xrightarrow{fast} ArN{:}N^+ + OH^-$$

The amine reacts in all cases in the unionized (i.e., basic) form, as is expected for an electrophilic substitution. The serious disagreements which are to be found in the earlier literature concerning the kinetic order of the reaction are almost entirely reconciled. It is observed that, under appropriate limiting conditions, the order with respect to amine is either zero or one, the order with respect to stoichiometric nitrous acid is one or two, and that distinct conditions exist where hydrogen ion, halide ion ($Hal^-$), and carboxylate ion are catalytically effective. The wide range of kinetic behaviour is due to the multiplicity of possible nitrozating agents. $H_2NO_2^+$, NOHal, and $N_2O_3$ were found to be effective under the experimental conditions. The species $HNO_2$ has to be brought into the scheme of things because the reagent is stored in that form; and the mixed anhydride Acyl·ONO, though scarcely effective as a nitrozating agent itself, is thought to be important because it can be an intermediate in the formation of $N_2O_3$ from $HNO_2$. It is suggested that some seemingly contradictory observations in the literature are to be attributed to the reaction between a buffer constituent (e.g., phosphate ion) and nitrous acid in one of its forms to produce a mixed anhydride.

The interconversion of these various forms of stoichiometric nitrous acid superimposes itself on the kinetics of the nitrozating act proper. Zero order with respect to amine arises whenever the generation of the effective nitrozating agent controls the rate, and high reaction orders occur when an established pre-equilibrium precedes the rate-controlling nitrozation. The following diagram summarizes the relevant interconversions



where the top route represents anion ($X^-$)-catalysis, the bottom route hydrogen-ion catalysis, and the middle route the uncatalysed reaction. The cation $NO^+$ which on general grounds is expected to be the most reactive nitrosating species, does not play a role in any of the mechanisms, presumably because it is not formed in the weakly acidic solutions studied. Neither is there any evidence for the intervention of the hypothetical species $HN_2O_3^+$.

Related studies of oxygen-isotope exchange (169, 170) and electronic absorption spectra (171) provide support for the reality of the equilibria postulated on the basis of the diazotization kinetics.

Several investigations add to the current discussions of the course of deaminations brought about by the agency of nitrous acid. Lewis advances further evidence that the slow step in the reaction of benzenediazonium ions with aqueous chloride solutions is the formation of free phenyl cations. The low selectivity of this species (in its reaction with chloride ions and with water) fits in with its high reactivity (172). The deaminations of $Me \cdot CH{:}CH \cdot CH_2 \cdot NH_2$ and of $CH_2{:}CH \cdot CHMe \cdot NH_2$ have been found to give different mixtures of the isomeric butenols; the unrearranged alcohol in each case is the major product. The result contrasts with the observation that the reactions of both the corresponding chlorides with silver acetate in acetic acid solution lead to the same mixture of products. The authors state that these observations add support to a current hypothesis that carbonium ions derived from diazonium ions by nitrogen loss are "hot," in the sense that they undergo substitution before rearrangement (173). As bond isomerism of free allylic cations is impossible (the two "isomers" corresponding to different arrangements of electrons), the "hotness" of the ion seems to be a result of its imperfect "freeness" which—because of the ultimate electrical neutrality of the leaving nitrogen molecule—causes the inverse of a "shielding" effect to operate.

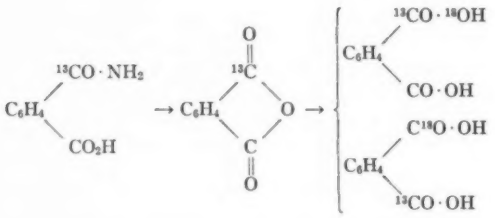
The deamination of $CH_3 \cdot CHPh \cdot CH(CH_3) \cdot NH_2$, isotopically labelled in one of the methyl groups, has been found to lead to the isotopic mixture of alcohols in which the label is equally distributed between the two methyl groups. The result rules out the occurrence of a concerted internal displacement reaction, in which phenyl migration and C—N bond rupture are synchronous (174). The authors interpret their observation in terms of the intermediate formation of symmetrical "phenonium" ions, but the results do not seem to exclude the possibility that equilibrium between two classical open carbonium ions is established prior to their destruction by the solvent. A searching consideration of reactions on this basis seems desirable in view of the increasing success with which the detailed stereochemical consequences of deaminations in related systems and also of other rearrangements (32, 175) are being explained by Collins *et al.* in terms of open ions.

The nitrous acid deamination of cyclic α-amino-alcohols has been examined, leading to conclusions concerning the stability of the carbonium ions involved in relation to their structure (176).

*Intramolecular catalysis.*—The notion that a neighbouring group can directly interact with a reaction centre and cause either an internal substitu-

tion ($S_Ni$) or a rate-enhancing stabilization of the transition state ("neighbouring-group participation," "synartesis," "anchimeric effect") plays a prominent part in contemporary schemes of reaction mechanisms (7). A related phenomenon is the unusual speed of hydrolysis of esters and amides derived from *ortho*-substituted benzoic acid or phenol.

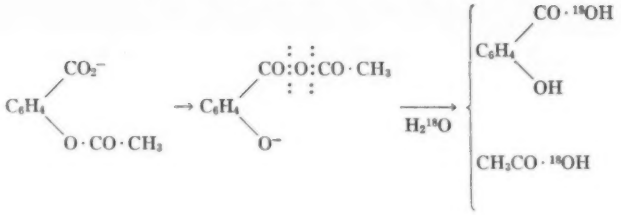
A typical example of this behaviour is phthalamic acid (177), the hydrolysis velocity of which is directly proportional to unionized amide in the pH range 1 to 5. At pH 3 the hydrolysis is about $10^5$ times faster than that of benzamide which, in turn, is somewhat more rapidly hydrolyzed than terephthalamic acid. The rate disparity rules out an interpretation based on electronic substituent effects and suggests a special interaction between the adjacent benzene substituents. The nature of the interaction was elucidated by an isotope experiment in which phthalamic acid labelled with $^{13}C$ in the amide group was hydrolyzed in $H_2{}^{18}O$. The resulting phthalic acid contained $—{}^{13}CO\cdot{}^{18}OH$, $—CO\cdot{}^{18}OH$ and $—{}^{13}CO\cdot OH$ groups, indicating a reaction intermediate which is symmetrical with respect to the two carbonyl groups. Phthalic anhydride has this required structure. The catalysis therefore consists of an internal substitution reaction forming the rapidly hydrolyzed intermediate phthalic anhydride. The course of the isotope experiment is thus



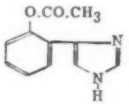

The corresponding external catalysis (acetic acid catalyzing the hydrolysis of benzamide) under comparable experimental conditions could not be detected, confirming the exceptional efficacy of the intramolecular catalysis.

Analogous results have been reported for methyl hydrogen phthalate where the carboxylate group catalyses an ester hydrolysis. The mechanism is again thought to involve phthalic anhydride as an intermediate. Here again the external catalysis (acetate ions catalyzing the hydrolysis of methyl benzoate) is barely, if at all, detectable (178).

The hydrolysis of the anion of aspirin (178), previously studied by several workers, probably involves a mixed anhydride as intermediate, as suggested by the observation that the hydrolysis products formed in $H_2{}^{18}O$ (salicylic acid and acetic acid) both contain $^{18}O$. This is explicable by the scheme

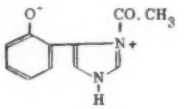


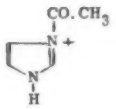
The corresponding intermolecular catalysis, although much weaker, is known in this case (acetate ions catalyzing the hydrolysis of aryl acetates) (178, 179). In fact, the hydrolysis of phenyl acetate is catalyzed by many kinds of bases (imidazoles, pyridines, anilines, and carboxylate ions). The Brønsted catalysis law is obeyed within each class, although here the function of the base clearly is not one of proton removal (179, 180). The intramolecular version of imidazole catalysis (181) has been realized with the very easily hydrolyzed derivative 3.



3.

In this case catalysis is thought to involve formation of the intermediate 4, by analogy with the intermediate 5,

4. 



5.

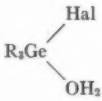
postulated for the intermolecular imidazole catalysis (180, 182) of the hydrolysis of phenyl acetate.

Other reactions which are considered to involve intramolecular catalysis are the stepwise hydrolysis of an aminoalkyl acetylsalicylate (183) and of the anion of monosalicyl malonate for which more complex forms of intermediate are thought to be formed (184). Examples of earlier work in the field and comparisons of intramolecular catalysis with hydrolytic enzyme action are given by Bender *et al.* (180, 185) and by Schmir & Bruice (181).

*Substitution reactions at atoms other than carbon.*—Two interesting contributions to the study of nucleophilic substitution reactions at elements other than carbon concern sulphur and germanium. It has been found that the speed of the exchange reaction

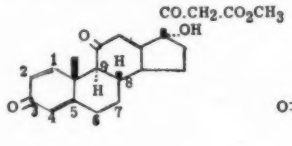
$$R—S—SO_3 + {}^*SO_3^= \rightarrow R—S—{}^*SO_3^- + SO_3^=$$

falls off along the series R = Me, Et, *iso* Pr, *tert* Bu in the same manner as the velocity of $S_N2$ reactions of alkyl halides of formula $R \cdot CH_2 \cdot Hal$. In both cases the largest rate decrease occurs with the last member of the series and is attributed to steric hindrance. The similarity of the two series of reactions points to a similar transition state structure, and it is suggested therefore that nucleophilic substitution in sulphur is an $S_N2$ reaction and involves a transition state in which entering and leaving groups and the central sulphur atom lie in a straight line (186). The solvolysis of triarylgermyl halides ($R_3GeHal$) has been found to be retarded by common halide ions, but the substituent effects (retardation by a *p*-methyl group) argue against a rate-determining ionization to $R_3Ge^+$. The results are interpreted in terms of the formation of an intermediate

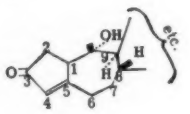



from which halide ion is lost in a subsequent reversible step (187). Both studies illustrate the utility of the application of Hughes and Ingold's classical mechanistic criteria outside their original field.

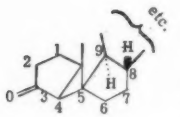
*Photochemistry.*—Recent years have seen a remarkable growth of interest in the chemical transformations taking place in comparatively complex organic molecules under the influence of visible or ultraviolet light, and in the establishment of the structure of the photochemical products by the methods of organic chemistry. The studies are typified by Barton and Taylor's work on prednisone acetate 6 which, on irradiation with ultraviolet light in aqueous acetic acid, ethanol, or hot dioxane, is transformed into the structures 7, 8, and 9a, or 9b, respectively (188). A rather simpler system is presented by the general photochemical cleavage in wet dioxane of cyclo-



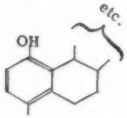

6.



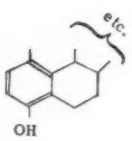

7.




8.

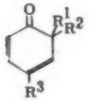



9a.




9b.

hexadienones of structure



to acids of the formula

$$R^1R^2 \cdot C{:}CH \cdot CR^3{:}CH \cdot CH_2 \cdot CO_2H \quad (189).$$

Experimental work of this kind is usually considered to be outside the orbit of physical chemistry. However, it is the writer's impression that studies in this general field mark the beginning of a nonspectroscopic approach to the structure and chemistry of electronically excited states, and that their consideration in relation to radiation chemistry and to electronic spectra and photochemical reactions of simple molecules promises to become an exciting subject for physical organic chemistry in the near future.

Perhaps it is not too foolish to draw a parallel here with the events in chemistry (190, 191) whose centenary was celebrated in 1958. The principles of chemical valency were recognized by Kekulé and Couper, not on the basis of intensive study of simple molecules but through the consideration of then apparently complicated chemical transformations of organic substances.

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# PROTEINS AND SYNTHETIC POLYPEPTIDES

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## INTRODUCTION

For many years chemists have been concerned with the structure of proteins and the relationship between structure and biological function. One of the earliest problems confronting the physical chemist was the elucidation of the over-all size and shape of the protein molecule in dilute aqueous solution. Preoccupation with this problem arose from the recognition that the polypeptide chains in both globular and fibrous proteins are folded in some manner, and from the realization that a crude estimate of the extent of such folding might be obtained from a knowledge of the over-all molecular size and shape. Thus, a large number of investigations have been carried out using such techniques as light scattering and hydrodynamic methods, and we now have extensive data which give information about the over-all dimensions of many protein molecules. The problems involved in the interpretation of such data have also received extensive discussion (35, 136, 153, 154, 181). However, during the last few years, the physical chemist has been able to probe beyond the bare outlines of the protein molecule, as embodied in the "size and shape" problem, and has been able to obtain considerable information about the internal configurations of proteins. The recent successes in this direction have arisen largely from x-ray diffraction studies of crystals of amino acids, peptides, and proteins, and from the application of optical, thermodynamic, and statistical mechanical methods to investigations of the solution properties of proteins and synthetic polypeptides. It is the purpose of this review to consider some of the information obtained about internal configurations and to emphasize some of the developments which have taken place since this subject was reviewed by Kauzmann (83).

The current working hypothesis about the internal structure of a protein regards the molecule as an assembly of organized and unorganized structures. One type of organized structure, about which much has been written (18, 22, 111, 122, 123), is the $\alpha$-helix of Pauling and Corey. While the existence of the $\alpha$-helix in both fibrous and globular proteins has not yet been proven conclusively, increasing evidence is being accumulated to support the Pauling-Corey suggestion. In those regions of the molecule where an organized structure does not exist, one can envisage a variety of possible configurations. The recent tendency has been to focus attention on one particular kind of disorganized structure, the random coil, which is the model used to interpret the solution properties of many synthetic polymers (41). The basic problems which have recently occupied the attention of the protein physical chemist are: the nature of the organized structure, the relative amounts of helix and random coil within a given protein molecule, and the conversion of one kind of structure into another. Synthetic polypeptides

have been investigated to obtain information pertinent to the protein problem.

Several years ago, Linderstrøm-Lang (106), regarding a helical structure as a likely part of the architecture of the protein molecule, proposed a useful nomenclature for considering the various configurational features of the organized part of the molecule. The polypeptide chain, in which the amino acid residues are linked together by covalent peptide bonds, is regarded as the primary structure. The folding of the peptide chain into a helix is a manifestation of the secondary structure of the molecule, and the interactions which link helices together comprise the tertiary structure. The classical work of Sanger (135), in the elucidation of the amino acid sequence of insulin, and of other workers in the determination of the amino acid sequences of other proteins [reviewed by Anfinsen & Redfield (1) and by Sorm (162)] are clear illustrations of the powerful attack which organic chemists have made on the problem of the primary structure. It is in the realm of the secondary and tertiary structures of proteins and synthetic polypeptides that the physical chemist has been able to contribute most, and it is these problems with which we shall be concerned. However, in passing, it is worth mentioning, in connection with the primary structure problem, the interesting kinetic studies which Katchalski (81, 82) has carried out for the synthesis of polypeptides, as well as the contributions of Craig (20, 21), Moore & Stein (118), Tiselius (188), and others who have provided the organic chemists with physical chemical methods for the separation of polypeptide fragments to facilitate their sequence studies.

## SECONDARY STRUCTURE

So much has been written about the α-helix of Pauling and Corey that we shall refer the reader to the literature for details of this and other helical structures (22, 111). Instead of presenting these details, we shall be concerned here with theoretical and experimental investigations of the relative stability of the helix compared to the random coil, and of the influence of the tertiary structure on the stability and on other properties of proteins. These problems have been considered in detail by Kauzmann (83), and we shall therefore concentrate on the more recent developments of the past two years.

### Theory of Stability of Helices

*Helix-random coil transformation.*—The first attempt to formulate a quantitative theory for the thermodynamics of the helix-random coil transformation was that of Schellman (143) whose results have been reviewed by Kauzmann (83). Among other things, Schellman's treatment involved estimations of the heat of formation of a peptide hydrogen bond in aqueous solution and of the configurational entropy of the randomly coiled polypeptide chain. Small changes in these parameters would not alter the general conclusion that the polypeptide chain must attain a critical size in order that

the helix be stable, and that the transition from a helical to a randomly coiled configuration may be treated thermodynamically as a first-order phase transition for sufficiently long chains. Of course, the details of the equilibrium depend on the numerical values used for the parameters. In particular, there is considerable uncertainty about the heat of formation of a hydrogen bond in a protein which is dissolved in water. From an analysis of the thermodynamics of aqueous urea solutions (143), Schellman has taken $\Delta H$ as $-1.5$ kcal./mole. However, the higher value of $-6$ kcal./mole (96) has given very good agreement between theory and experiment in a variety of protein reactions such as ionization (96, 110), association (36, 176), and denaturation (94). In addition, Warner (191) has found a value of $-4$ to $-4.5$ kcal./mole from experiments on polynucleotides. A preliminary attempt to determine $\Delta H$ from model compounds such as the hydroxybenzoic acids also leads to a value of about $-6$ kcal./mole (66, 67). It would be very desirable to have further experimental determinations of this important parameter for a variety of compounds.

Recently, more elegant models and mathematical treatments have been applied to the problem of the helix-random coil transformation (55, 56, 74, 124, 125, 132, 146, 202, 203). In these statistical mechanical theories[1] the helix is considered as a one-dimensional array of amino acid residues with the possibility of formation of the peptide hydrogen bonds at any part of the chain, the chain ends constituting a special case, as already pointed out by Schellman (143). There is a geometrical restriction that three successive hydrogen bonds must be ruptured to produce a break in the helix. Subject to this restriction one must count the number of ways in which ruptured and unruptured peptide hydrogen bonds can be distributed along the whole polypeptide chain. This is essentially the problem of a one-dimensional Ising lattice which has been used as a model for the theory of ferromagnetism, wherein the spins can be aligned parallel or antiparallel. The various theories differ in the manner in which the partition function is generated and used to obtain the thermodynamic functions to characterize the transition. However, all the theories lead to the conclusion that a sharp transition is possible in this one-dimensional system for very large chain length and for hydrogen bond energies above a critical value. For short chain lengths and reasonable values of the parameters, the transition appears similar to but not actually identical with a first-order phase transition, i.e., the transition is somewhat diffuse, taking place over a small finite range of temperatures. The disordering effect of the chain ends in Schellman's theory (143) appears in the theory of Zimm & Bragg (202, 203), for example, as a nucleation process. While one-dimensional lattices in general (90), and a one-dimensional Ising lattice in particular (73, 119), do not show a phase transition, Zimm & Bragg point out (202) that "this transition does not really violate the Landau and Lifshitz proof (90); the question is more what is meant by the word 'phase.' Their proof

[1] I am indebted to Drs. B. Widom and B. H. Zimm for helpful discussion of these theories.

merely shows that in a one-dimensional system the regions of exclusively one phase cannot be large; but rather the preferred configuration consists of many small regions alternating between the two phases, whereas we have shown that such a situation can still lead to a reasonably sharp transition with change of temperature." Thus, because of a gain in entropy of mixing between small crystalline regions and amorphous regions, the Landau-Lifshitz theorem accounts for the result that the helices will not be too long, i.e., breaks will occur; but this broken helix can show a fairly sharp phase transition. While the statistical mechanical theories give essentially the same results obtained earlier by Schellman (143), the new treatments shed light on the details of the configurations to be expected under given conditions, e.g., the number of breaks in a long helix and the amount of disorder at the ends. Details of these various theories, most of which were presented at the September, 1958, meeting of the American Chemical Society, must await their publication.

*Elastic mechanisms in fibrous proteins.*—A theory of the helix-random coil transformation is also embodied in Flory's recent treatment of elastic mechanisms in fibrous proteins (43). However, Flory's treatment is not restricted to the $\alpha$-helix but applies to any ordered or crystalline state such as those involving intramolecular hydrogen bonds. Flory assumes that the shrinkage of a fibrous protein, such as collagen, or the denaturation of a fibrous or globular protein, involves transitions between crystalline and amorphous phases (42, 43, 44). In the melting process there is a contraction in the fiber, resulting in a retractive force. The contraction arises because the polypeptide molecule in the random configuration (amorphous form) has a length, projected on the fiber axis, which is less than its length in the crystalline state. If cross-linkages, such as disulfide bonds which survive during the melting process are present, they are considered to have been superimposed on the crystalline state. Thus, after melting, the random coil is cross-linked in a nonrandom fashion.[2] As a consequence of this nonrandom cross-linking of the random coil, the elastic properties of the latter will differ from those of an amorphous polymer which has been cross-linked in the amorphous state. Specifically, with nonrandom cross-linking, the amorphous state will have a lower entropy since fewer configurations are available to it because of the constraints of the cross-links.

The equilibrium retractive force, $f$, depends on temperature, $T$, according to the equation

$$[\delta(f/T)/\delta(1/T)\,]_P = \Delta H/\Delta L \qquad 1.$$

[2] This is in contrast to the network structures in synthetic polymers which have been formed by introducing cross-links when the molecules are in the random coil form. However, if the chains of a synthetic polymer are first ordered and then cross-linked [e.g., racked rubber (121, 133, 134), where ordered chains are cross-linked by gamma irradiation], the situation is analogous to that existing in the cross-linked crystalline fibrous protein.

where $\Delta H$ and $\Delta L$ are total changes in enthalpy and length, respectively, upon melting the crystalline sample (43). Equation 1 is an analog of the Clapeyron equation. If the fiber is immersed in an excess of solvent, then $\Delta H$ and $\Delta L$ contain contributions not only from the fusion of the pure crystalline form but also from the integral changes for mixing of the solvent with the amorphous polymer to form the mixed phase at the given equilibrium concentration. Equation 1 pertains to the situation where both crystalline and amorphous phases coexist in equilibrium, the equilibrium force being independent of the fiber length at constant $T$ and $P$.

Making use of the stress-strain relation for oriented noncrystalline fibers, Flory related the amorphous length to the force and integrated equation 1 to obtain a relationship between $f$ and $T_m$, the latter being the melting point, or transition temperature, at a force such that the amorphous length is $L^a$. This relationship takes on a simple form if the deformation is sufficiently large, i.e., if $L^a$ is much greater than the length at zero force. In such a case, the integrated form of equation 1 becomes

$$f/T_m = (3k\nu n'/L_m)\left[L^c/L_m \pm \sqrt{(2\Delta h'/3R)(1/T_m - 1/T_m^c)}\right]. \qquad 2.$$

where $k$ is the Boltzmann constant, $\nu$ is the total number of chains in the network structure, $n'$ is the number of statistical segments per chain, $L_m$ is the length of the fiber at maximum extension, $L^c$ is the length of the sample when totally crystalline ($\Delta L = L^a - L^c$), $T_m^c$ is the melting point when $L^a = L^c$, $R$ is the universal gas constant, $\Delta h' = N_a \Delta H/\nu n'$, and $N_a$ is Avogadro's number. The application of the Flory theory to the elastic properties of collagen will be considered below.

In summary, the various theories predict a first-orderlike phase transition in the transformation from a helix to a random coil. The relative stability of the helical form over that of the random coil (i.e., the standard free energy change for the transformation) will depend on the balance between the heat of formation of the peptide hydrogen bonds and the loss of the configurational entropy of the randomly-coiled chains. Some discussion about the heat of formation in aqueous solutions has already been presented. As for the configurational entropy, Schellman (143) has made some estimates of this quantity, and Flory has provided a statistical mechanical treatment on the basis of a lattice model (41). These authors have also calculated the entropy change due to the introduction of cross-links which stabilize the crystalline form. Flory's result (43) is:

$$\Delta S = -R\nu[(3/4)\ln n' + 9/4] \qquad 3.$$

Schellman's result (143) is similar. If the side chains can form hydrogen bonds when the polypeptide chain is in the helical form, then additional stability will be provided for the helix. This problem is considered in later sections in which we shall consider the influence of the tertiary structure on the stability of the secondary structure.

## Methods of Investigation

There are several experimental methods which have been used to investigate the presence of helical and randomly coiled structures in proteins and synthetic polypeptides, and the relative amounts of helix and random coil forms in a given molecule. Hydrodynamic and light scattering data have been used to decide whether a given polypeptide structure is a helix or a random coil. Once the structure was established, it has served as a model in order to assess recently developed methods for the study of internal configuration. Three of the most commonly used techniques (deuterium-hydrogen exchange, infrared absorption spectra, and optical rotatory power) have previously been reviewed by Kauzmann (83). Some recent applications of these methods will be discussed and two other methods will be considered, namely, the study of the elastic properties of protein fibers and the study of possible tertiary hydrogen bonds compatible with the postulated helical structure.

## Helix-Random Coil Transitions in Synthetic Polypeptides

By a suitable choice of solvent it is possible to provide a favorable heat of formation of the peptide hydrogen bond to permit the existence of stable helices. This method has been adopted by Blout, Doty & co-workers (8, 29, 200) who used viscosity, flow birefringence, light scattering, and optical rotation measurements to follow the transformations, primarily in synthetic polypeptides. More recently Yang (198) has applied the technique of non-Newtonian viscosity (147) to the problem. Much of the pioneering work in this field has already been reviewed by Kauzmann (83).

Very recently Blout, Doty & co-workers (3, 27, 28, 30, 32) have considered the effect of pH on the configurations of polypeptide helices containing ionizable groups. Poly-L-glutamic acid was investigated in 0.2 *M* NaCl-dioxane (2:1) as a function of pH (30, 32). At low pH, where the carboxyl groups are in the COOH form, a sample of molecular weight 34,000 was in the helical configuration. In the pH range of 5.4 to 6.4, beginning when about 40 per cent of the COOH groups are ionized, a transition to a random coil form occurs. Doty & co-workers suggest (32) that the helical configuration cannot withstand the electrostatic repulsion due to the accumulation of charge. However, they point out that hydrogen-bonded COOH groups could stabilize the helix. Thus, the transition may be due not only to electrostatic repulsions but also to the rupture of these side-chain hydrogen bonds, if present. Poly-L-lysine behaves in a similar manner (3, 30), being helical above pH 10.5 where all the $NH_3^+$ groups have dissociated protons, and randomly coiled below this pH, presumably due to electrostatic repulsions. Doty & co-workers have not considered the possibility that the helix could be stabilized in the transition region by $NH^+ \cdots N$ side-chain hydrogen bonds. Equimolar copolymers of L-lysine and L-glutamic acid were also investigated (30). The copolymer has a maximum helical content in acid solution, diminishing as the pH is raised. Doty & co-workers suggest that helix

stabilization at low pH may be due to hydrogen bonding between pairs of glutamic acid residues on adjacent turns of the helix. Apparent p$K$'s of 4.5 and 10.5 were obtained from titration data. It was concluded (30) that these values are normal ones for carboxyl and amino groups, with no discussion given of possible effects of electrostatic or side-chain hydrogen bonding interaction. The helical structure at low pH is diminished but not eliminated by 8 $M$ urea.

In these investigations the primary technique was that of optical rotary dispersion. Whereas the earlier experimental work had been interpreted in terms of theoretical results of Moffitt (32, 115, 117, 199), a comparison (116) of Moffitt's theory with that of Fitts & Kirkwood (38, 39) led to the discovery of an error and also the realization that further terms arising from electronic transitions in the chromophores had to be evaluated in order to correctly account for the dispersion data. Fitts & Kirkwood (40) have evaluated these terms and find agreement with data of Doty & Lundberg (31) on the dispersion due to the helices. However, Doty (27) raises the question as "to what extent the agreement is fortuitous because numerically large terms of opposite sign are involved in the summation." In view of the present situation with regard to the theory of optical rotation [see also Schellman (144)], Doty (27) prefers to treat the dispersion data from an empirical point of view.

Since one of the consequences of the theories previously discussed is the prediction of a critical size before the polypeptide chain can exist in a helical form it is of interest to confirm this prediction experimentally with synthetic polypeptides. The critical size cannot be predicted very accurately because of the uncertainties in the values of $\Delta H$ and $\Delta S$ for the formation of a peptide hydrogen bond, as already discussed. Nevertheless, within these limitations, Schellman (143) suggests that a helix should contain 8 to 15 units before it can achieve stability in water (without any contributions from the side-chains or from disulfide cross-links). The only experiments on synthetic polypeptides carried out thus far were performed in nonaqueous solvents rather than in water. Preliminary studies with poly-$\gamma$-benzyl-L-glutamates of varying chain length have led to an experimental estimate of the critical degree of polymerization of between 7 and 14 in dioxane and dimethyl formamide solutions (114). These values are only approximate, since the samples studied were not well fractionated. It would be extremely useful for checking the values assigned to $\Delta H$ and $\Delta S$ of hydrogen bond formation to have an experimental determination of the critical size in water. The influence of the side-chains and disulfide cross-links will have to be taken into account (63) in predicting the critical size. For example, such interactions (or their absence) very likely play an important role in aqueous solutions of the oxidized A-chain of insulin (78, 109) and of oxidized ribonuclease (63). The former has 21 residues and the latter 124, yet both are devoid of helical structure. The oxidized B-chain of insulin, consisting of 30 residues, shows a slow deuterium-hydrogen exchange (100), suggesting the possible presence of

helical portions in the molecule. However, the slow exchange is probably the result of aggregation (100); presumably, if the molecules were nonaggregated they, too, would be in the randomly coiled form. Thus, these fairly long polypeptide chains are not helical in water, perhaps because of the absence of favorable side-chain or disulfide cross-linking interactions. Change of solvent, e.g., to concentrated lithium bromide (64), produces a greater degree of folding of oxidized ribonuclease, probably because of a more favorable heat of formation of the peptide hydrogen bond in this solvent, and possibly because of a diminution of electrostatic repulsion.

It is of interest to mention a helical structure in which a polypeptide chain can exist, even without the possibility of forming N—H · · · O=C hydrogen bonds. An example of such a helix is poly-L-proline (19, 37) where hydrogen bonding is not possible because the imide nitrogen of the proline ring is devoid of a hydrogen atom. The chain is capable of being maintained in a helical configuration because of steric restraints. Two forms of the chain are known and their interconversion has been studied by Harrington & Sela (65) with the aid of optical rotation, viscosity, and sedimentation measurements, and also by Fasman & Blout (37). In aqueous solution polyproline I exists as a right-handed helix with peptide bonds in the *cis*-configuration whereas polyproline II exists as a left-handed helix with peptide bonds in the *trans*-configuration. Polyproline I mutarotates in water to polyproline II over a period of several days (89).

Interesting steric effects can be superimposed on the α-helix itself. It is possible that the large side-chain groups in poly-L-histidine and poly-L-tyrosine can arrange themselves in the form of a second helix outside that composed of the backbone chain. Preliminary experiments on the rotary dispersion of these polymers indicate that such a concentric pair of helical structures may exist (27).

The examples cited here are illustrative of the kinds of helix-random coil transformations which can occur in synthetic polypeptides. Similar transformations in proteins will be considered in subsequent sections.

## Helical Structures in Proteins

*Elastic properties of fibrous proteins.*—Flory's theory discussed above has been applied to the thermal shrinkage of rat-tail collagen (33, 46, 120, 164), a process which has been shown to involve a first-order transition between crystalline and amorphous (shrunken) phases (42, 54). The collagen fibers were tanned with formaldehyde or with quinone to cross-link them and then clamped in a dynamometer in the presence of excess solvent. The system was brought to various temperatures and the equilibrium force was measured. The latter was found to be substantially independent of the fraction of the fiber shrunken, as predicted by theory. At each temperature there was coexistence of both crystalline and amorphous phases, so that equation 1 or its integrated form were applicable to relate $f$ to $T$. After correction for the

heat of dilution of collagen, estimated from the temperature coefficient of the degree of swelling in the amorphous state, a value of about 1.5 kcal. per mole of peptide units was obtained for the latent heat of fusion. In support of the applicability of equation 1 to collagen (i.e., as proof that the thermal shrinkage of collagen is a first-order phase transition), Flory & co-workers point out (120) that this value of $\Delta H$ is in good agreement with values obtained from calorimetric measurements and also from measurements of the depression of the melting point of collagen by glycol. A similar successful application of the theory has been made (121) in the thermal shrinkage of racked rubber, cross-linked by gamma radiation. The latter system consists of randomly-coiled, long-chain polymers which are capable of crystallizing when stretched, the cross-links being introduced in the stretched state. The physical picture, embodied in the application of equation 1 to these experiments on collagen and racked rubber, may be envisaged as follows. At a given temperature a certain force is required to maintain equilibrium between crystalline and amorphous phases. If the temperature were to be raised, the crystalline phase would become unstable and melt. In order to prevent melting, i.e., to preserve equilibrium between the two phases at the higher temperature, the force must be increased, as indicated by equation 1. The increased force keeps the chains in an extended configuration to enhance the stability of the crystalline form. Flory & co-workers (46) suggest that similar phase transitions are involved in dimensional changes of other fibrous proteins. Preliminary data on fibrin fibers (152) appear to confirm this suggestion. Similarly, dilatometric studies of Flory & Garrett (45) indicate first-order phase transitions not only in collagen but also in the melting of gelatin gels. These transitions are analogous to those of Blout, Doty & co-workers, as discussed earlier, wherein dissolved polypeptide helices transform in suitable solvents to random coils over a small range of temperatures. Since the equilibrium state corresponds to a situation in which the free energies of the crystalline and amorphous forms are equal, any variable (such as temperature, pH, or change of solvent), which affects the free energy of either form, can be altered to produce a helix-random coil transition.

*Determination of secondary structure from side-chain interactions.*—Another method for studying secondary structure involves the location of specific tertiary bonds (disulfide, hydrogen, or hydrophobic bonds). This method may be illustrated using insulin as an example, since the amino acid sequence of this protein is known. Insulin contains three disulfide bonds, one in the A-chain and two connecting the A- and B-chains (135). Whatever folding is postulated for the secondary structure, proper account must be taken of the known location of the disulfide bonds. If, in addition, two or three specific interactions, e.g., hydrogen bonds, could be demonstrated to exist between certain side-chain groups of the molecule, the number of possible ways of folding the polypeptide chains would become severely restricted and the secondary structure would be determined thereby. Hence, this approach to

the study of the internal structure involves the performance of experiments designed to demonstrate the existence of specific side-chain hydrogen bonds. For this purpose it is very useful to have available a set of molecular models to be able to envisage which side-chain groups might be near enough to interact. Later we shall present experimental studies connected with possible hydrogen bonding of lysyl and tyrosyl side-chains in insulin. This method is, in principle, applicable to any protein. However, for obvious reasons, its usefulness will be limited to those proteins whose amino acid sequence is known.

## X-ray Diffraction Studies of Myoglobin

Whereas x-ray diffraction studies of protein crystals have been carried out for many years (22), the complete determination of the structure of a globular protein has not yet been achieved. However, considerable progress has recently been made, and a brief discussion of the results of Kendrew (84) on the structure of myoglobin is in order at this point.

The recent successes are primarily the result of the solution of the age-old phase problem in x-ray diffraction by the method of isomorphous replacement. A description of this method has been given by Crick & Kendrew (22). This technique has been applied by Perutz & co-workers (57) to the hemoglobin problem, by Harker & co-workers and by Carlisle & co-workers (quoted in 22) to the ribonuclease problem, and by Kendrew (84) to the myoglobin problem. A low-resolution investigation of chymotrypsinogen has been reported by Kraut (86).

Myoglobin consists of 153 amino acid residues, linked together in a single chain, and a prosthetic heme group. X-ray diffraction pictures were taken of crystals of myoglobin and of each of five different metal-substituted myoglobins. In order to avoid the problem of measuring a large number of reflections, Kendrew limited his resolution to 6 A. Thus, in his final structure he could not resolve individual atoms which are 1 to 2 A apart. However, at a resolution of 6 A, the compact configuration (e.g., $\alpha$-helix) of the polypeptide chains could be seen without resolution of the side-chains. Having resolved the phase problem it was possible to obtain a three-dimensional representation of the density of matter throughout the unit cell at the 6 A resolution. The rodlike features which appear in this representation are regarded as blurred representations of the polypeptide chains, in a helical configuration. Adding up all the visible lengths of rod, Kendrew could account for two-thirds of the whole molecule, as well as for the location of the heme group containing the heavy iron atom. On the basis of these results Kendrew was able to construct a model of the myoglobin molecule. The molecule is compact with approximately 70 per cent of its length in a helical configuration. More details of the structure will become available if the many extra reflections required to obtain a 2 A resolution can be computed. Even at the 6 A resolution, the picture obtained is consistent with that obtained from studies of secondary structure of proteins dissolved in aqueous solution.

### Tertiary Structure

As already indicated, the tertiary structure may play a role in which it contributes to the stability or instability of helical secondary structures. The principal kinds of interaction in the tertiary structure are disulfide bonds, hydrogen bonds, and hydrophobic bonds. As pointed out elsewhere (96), salt bridges between $NH_3^+$ and $COO^-$ groups may be considered as hydrogen bonds. Very little theoretical or experimental work has thus far been carried out on hydrophobic bonds in proteins. One example of such bonding is the methyl-methyl interaction which stabilizes the helical configuration of poly-D,L-alanine (6, 107). Our discussion here will be concerned primarily with side-chain hydrogen bonding, with a brief consideration of disulfide bonds.

Besides contributing to the stability of helical structures, side-chain hydrogen bonding can influence any kind of protein reaction which involves the side-chains, e.g., binding of small ions and molecules, limited proteolysis, protein-protein association, denaturation, etc. Therefore, we shall consider first, from a theoretical point of view, the thermodynamics of formation of such side-chain hydrogen bonds and their influence on protein reactions, and secondly, some experiments to locate specific side-chain hydrogen bonds in protein molecules.

### Acid-Base Equilibria

Since most of the polar side-chain groups have p$K$'s which permit them to dissociate protons in an experimentally accessible pH range, it is worthwhile to consider the acid-base equilibria of these groups before taking up the question of hydrogen bonding. This subject has recently been treated in great detail by Linderstrøm-Lang & Nielsen (108) and only a brief summary will be presented here.

The first fairly successful theory for the interpretation of the titration curve of a globular protein was that of Linderstrøm-Lang (105). The model used is a rigid, impenetrable sphere of low dielectric constant with the net charge uniformly distributed on the surface and immersed in a medium having the dielectric constant of water. A statistical treatment is used to take account of the fact that the protein can contain several types of ionizable groups of widely different p$K$'s (e.g., carboxyl and amino groups). However, all groups of a given kind are assumed to be intrinsically identical. In addition to the statistical problem, the electrostatic interaction between the dissociating group and the rest of the charges in the molecule is calculated. Aside from the electrostatic interaction, all the groups are assumed to be independent of one another. The titration curve may then be computed in terms of $r$ as a function of pH, where $r$ is the number of moles of hydrogen ion dissociated, per mole of protein, at any pH. The value of $r$ is usually taken equal to zero at the pH of maximum proton binding. If $r_i$ is the corresponding quantity for the $i^{th}$ type of group, then at any pH

$$r = \sum_i r \qquad 4.$$

If there are $n_i$ of the $i^{th}$ type of group and at any pH $r_i$ of these are in the form of the conjugate base, then Linderstrøm-Lang's result may be expressed (177) as

$$\log \frac{r_i}{n_i - r_i} = \text{pH} - (\text{p}K^\circ)_i + \frac{2Zw}{2.303} \qquad 5.$$

where $(\text{p}K^\circ)_i$ is the intrinsic dissociation constant for the $i^{th}$ type of group, $Z$ is the average net charge on the protein, and $w$ is a factor which contains the electrostatic interaction and is given by the expression

$$w = \frac{N\epsilon^2}{2DRT}\left[\frac{1}{b} - \frac{\kappa}{1 + \kappa a}\right] \qquad 6.$$

where $N$, $R$ and $T$ have their usual meaning, $D$ is the dielectric constant of the solvent, $\epsilon$ is the electronic charge, $\kappa$ is the inverse of the radius of the ionic atmosphere, and $b$ and $a$ are the hypothetical radii of the molecule and of exclusion, respectively. In this treatment, the titration curve of the protein is a superposition of the curves for the various types of groups.

This theory has had unusual success despite the unrealistic assumptions involved. Linderstrøm-Lang & Nielsen (108) attribute the success for some proteins to a fortunate compensation of effects wherein "the assumption of randomly distributed charges overestimates the real charge-charge interaction to approximately the same degree as the use of the bulk dielectric constant of water underestimates it."

Several attempts (70, 71, 72, 179) have been made to improve the Linderstrøm-Lang model for the interpretation of titration curves of proteins. We shall consider briefly the recent treatment of Tanford & Kirkwood (184). Instead of considering the charges as uniformly distributed on the surface of a sphere, these authors treat the charges as discrete ones at fixed positions near the surface of a sphere whose dielectric constant is taken as 2. In the evaluation of the electrostatic work to charge in the various protein species Tanford & Kirkwood neglect parts of the electrostatic interaction, claiming that this approximation corresponds to a model which is still considerably superior to the smeared-charge model of Linderstrøm-Lang. In a second paper, Tanford (180) has applied this approximation to calculate the titration curves for simplified model molecules, i.e., ones with discrete numbers of charges assigned to various geometrical arrangements within the protein molecule. He finds the result that a clustering of charges of a given sign about a dissociable group can have a significantly different electrostatic effect than would be observed if the charges were smeared out uniformly on a sphere, i.e., equations 5 and 6 fail to apply. Tanford's calculations serve the useful purpose of showing the approximate magnitudes of the deviations from the smeared-out model. It should also be mentioned that Tanford obtains reasonable results only if the charged sites are placed at about 1 A below the surface of the sphere. A discussion of the crucial nature of this ad-

justable distance parameter is given by Tanford (180) and by Linderstrøm-Lang & Nielsen (108). Subject to this difficulty, the results of Tanford show that various electrostatic models can be envisaged in order to account for the "abnormalities" of some protein titration curves. The latter have heretofore been said to be "abnormal" if equations 5 and 6 of the Linderstrøm-Lang model did not apply. It should be noted, however, that if equations 5 and 6 are assumed valid, it is possible in some cases (110) to account for the abnormality in terms of side-chain hydrogen bonding (96) instead of in terms of local electrostatic interactions. It then becomes a question how to decide whether a given abnormality is due to local electrostatic effects or to specific hydrogen bonding of the dissociable groups. The subsequent discussion of hydrogen bonding may provide some criteria for making this choice.

## Theory of Side-chain Hydrogen Bonding

*Thermodynamics of hydrogen bond formation.*—Having discussed the acid-base equilibria in which dissociable groups are involved, we can now turn our attention to the influence of hydrogen bonding between the polar side-chain groups on a variety of protein reactions. Since the effect of the hydrogen bond is superimposed on the electrostatic effect, a calculation of the former effect does not depend on the model assumed for the electrostatic interaction. However, for convenience, the Linderstrøm-Lang smeared-charge model is used, e.g., to see how the hydrogen bond modifies the p$K$'s. Whatever the kind of reaction in which these hydrogen-bonded groups are involved, it is first necessary to have some knowledge of the thermodynamic parameters for the formation of side-chain hydrogen bonds. These have been evaluated (96) by regarding the side-chain groups to be attached to rigid structures (e.g., the helically-folded backbone) and constrained within limits to interact only with neighboring side-chain groups. When the groups are free, there is the possibility of torsional oscillation about the single bonds in the side-chains. These oscillational degrees of freedom are considered to be lost when two side-chain groups interact to form a hydrogen bond. The thermodynamic parameters for the formation of a hydrogen bond between an $i^{\text{th}}$ donor and a $j^{\text{th}}$ acceptor have been estimated (96) as $\Delta H^\circ_{ij} \approx -6$ kcal./mole,

$$\Delta S^\circ_{ij} \approx -20 \text{ to } -30 \text{ e.u., and } \Delta F^\circ_{ij} \approx 0$$

(corresponding to an equilibrium constant $K_{ij} \approx 1$). Such a single bond between donor and acceptor groups of chemically distinct species has been designated as a heterologous single hydrogen bond (e.g., a tyrosyl · · · carboxylate ion bond). Other types of bonds may also exist, e.g., the homologous double hydrogen bond such as the COOH · · · HOOC bond in acetic acid dimers. Theoretical thermodynamic parameters for a number of types of hydrogen bonds have been evaluated (96).

*Modified reactivity of polar side-chain groups.*—The effect of these different types of hydrogen bonds on various protein reactions may now be examined. For example, the ionization of a tyrosyl group is modified if the

group is hydrogen bonded to some acceptor, leading to the following parameters (96) in a pH range where the acceptor group does not associate protons.

$$\Delta F^\circ_{obs} = \Delta F^\circ_1 + RT \ln (K_{ij} + 1) \quad 7.$$

$$\Delta H^\circ_{obs} = \Delta H^\circ_1 - \frac{K_{ij}}{K_{ij} + 1} \Delta H^\circ_{ij} \quad 8.$$

$$\Delta S^\circ_{obs} = \Delta S^\circ_1 - R \ln (K_{ij} + 1) - \frac{K_{ij}}{K_{ij} + 1} \frac{\Delta H^\circ_{ij}}{T} \quad 9.$$

where $\Delta F^\circ_1$, $\Delta H^\circ_1$, and $\Delta S^\circ_1$ are the parameters for the ionization of a non-hydrogen bonded tyrosyl group, including the electrostatic contribution, and $\Delta F^\circ_{obs}$, $\Delta H^\circ_{obs}$, and $\Delta S^\circ_{obs}$ are the observed values when the tyrosyl group is hydrogen bonded. The additional terms in equations 7, 8, and 9 arise from the hydrogen bond. These equations have been applied to data of Tanford for the ionization of tyrosyl groups in bovine serum albumin in order to evaluate the various parameters. Taking $\Delta F^\circ_{obs}$ as 14.1 kcal./mole and $\Delta F^\circ_1$ as 13.1 kcal./mole, equation 7 yields a value of 4 for $K_{ij}$, which is in good agreement with the theoretical value of unity. Using this value of $K_{ij}$, together with the values $\Delta H^\circ_{ij} = -6$ kcal./mole, $\Delta H^\circ_1 = 6$ kcal./mole, and $\Delta S^\circ_1 = -23$ e.u., the values of Table I were obtained (110) from equations 8 and 9. These are in good agreement with the experimental values.

TABLE I

COMPARISON OF EXPERIMENTAL AND THEORETICAL PARAMETERS FOR TYROSYL IONIZATION IN BOVINE SERUM ALBUMIN (110)

| | Theoretical | Experimental |
|---|---|---|
| $\Delta H^\circ_{obs}$, kcal./mole | 11 | 11.5 |
| $\Delta S^\circ_{obs}$, e.u. | −10 | −9 |

In general, depending on the pH, the acceptor group may also associate protons, and the resulting equations will be a bit more complex. Also, other types of hydrogen bonds (e.g., homologous double bonds) are characterized by more complex equations (96), leading to a variety of effects in titration curves quite different from those expected from equations 5 and 6.

The species being bound (designated as B) to the donor and acceptor groups may be a small ion or molecule other than a proton. In such cases, the hydrogen bond will affect the binding properties between B and the protein. For example, Carsten & Eisen (13) found that the observed association constant for the binding of substituted 2,4-dinitrobenzenes by serum albumin decreased as the amount of material bound increased. This may be explained (96) if B can bind to either of two donors $D_1H$ and $D_2H$ which in turn compete for a single hydrogen bonding acceptor A. As another example, the observed association constant can increase as the amount of material bound increases if the binding sites are involved in cooperative hydrogen

bonding (96). Such behavior has sometimes been observed, e.g., by Karush (79) and by Warner & Weber (192). The reader is referred to the original paper (96) for the mathematical details.

The hydrogen-bonding theory has recently been used to treat binding data for several different kinds of B groups, e.g., binding of potassium and sodium ions to myosin A, myosin B and actin, and binding of chloride ions to bovine serum albumin (104, 137, 138). In the case of serum albumin, Scatchard, Coleman & Shen (140) investigated the binding of a variety of anions with the aid of electromotive force measurements in cells containing ion exchanger membranes. Analysis of the data for the binding of anions to isoionic albumin on the basis of electrostatic theory indicated that there are three groups of sites, each with a different binding constant and with a different number of sites per group. In view of the possibility of considerable internal hydrogen bonding between the carboxyl and other side-chains of serum albumin (110), the binding data of Scatchard, Coleman & Shen (140), which indicate an apparent decrease of the binding constant with increasing amount of anion bound, might equally well be interpreted in terms of competitive side-chain hydrogen bonding, as discussed above for the data of Carsten & Eisen. An analysis of these data has been carried out by Saroff (138) who took into account not only the electrostatic effects but also hydrogen bonding between carboxylate ion and cationic groups. While Saroff was able to fit both the chloride and hydrogen binding data in the pH region 2 to 5 with this model, his electrostatic parameters (see equation 6) were somewhat different from those usually used for serum albumin. This could be due to an incomplete description of the internal hydrogen bonding or to a failure of the simple Linderstrøm-Lang model for the electrostatic effects, as already discussed. Both hydrogen bonding and electrostatic effects are probably involved in the binding of ions to proteins, especially when nonlinear $\nu/\alpha$ vs. $\nu$ plots are obtained ($\nu$ being the average number of ions bound per protein molecule and $\alpha$ being the activity of free ion), and both effects should be taken into consideration in interpreting binding data.

Whereas the side-chain groups comprising the binding site may be hydrogen-bonded, with a consequent effect on the binding properties, it does not necessarily follow that all small ions necessarily bind to single side-chain groups. Many side-chains may co-operate in the formation of a binding site, and it is important to have information on the relative positions of the various side-chain groups with respect to one another. Peticolas & Klotz (127) have carried out experiments to obtain information on the relative positions of side chains to which various ions are bound. They used as a yardstick a series of bifunctional azo dyes with varying distances between the two functional groups, and found that maximum binding to human serum albumin took place when both of the functional groups were 12 A apart. Significant variation of this distance in the azo dye molecule led to a decrease in the two-site binding.

The anomalies at low pH in the binding of protons and other small ions

and molecules to bovine serum albumin, and also in the hydrodynamic properties, have been investigated by a number of workers (2, 10, 11, 12, 14, 15, 16, 48, 49, 50, 60, 62, 87, 88, 102, 110, 129, 130, 131, 139, 140, 141, 155, 175, 182, 201). There seems to be a configurational change (201) accompanied by a co-operative transition (48) for which possible transitions in side-chain hydrogen bonding have been proposed (110). As pointed out by Foster & Aoki (48), the theory of the co-operative transition (48) and the theory of side-chain hydrogen bonding (110) are in "agreement that factors other than expansion (i.e., pure electrostatic effect as embodied in the $w$ factor) are responsible in large part for the titration anomaly in plasma albumin." This statement supersedes an apparent earlier disagreement on this question between the two theories (47, 110).

The low-pH expansion encountered in serum albumin seems to occur also in other proteins, e.g., conalbumin (128, 197). In some cases (e.g., $\beta$-lactoglobulin) dissociation is observed (187, 189, 190) in acid solution.

*Limited proteolysis.*—Tertiary hydrogen bonds can play an important role in limited proteolysis (97), e.g., in the thrombin-fibrinogen reaction (151) or in the activation of zymogens (58). If a peptide fragment is liberated from a protein by hydrolysis of a peptide bond, this reaction would be expected to go to completion on the basis of studies of equilibria in simple peptides (23), i.e., the hydrolysis constant, $K_{pep}$, for simple peptides is very large. However, if liberation of this fragment also involves the rupture of side-chain hydrogen bonds, then it may happen (97) that the observed hydrolysis constant $(K_{pep})_{obs}$ is significantly lower than $K_{pep}$, i.e., the hydrolytic reaction may not go to completion. The observed thermodynamic parameters (carrying "obs" subscripts) would differ from those to be expected for the hydrolysis of simple peptides according to the following equations, which are analogs of equations 7, 8, and 9, and show the contributions from the hydrogen bonds (97).

$$(\Delta F^\circ_{pep})_{obs} = \Delta F^\circ_{pep} + RT \sum \ln (K_{ij} + 1) \qquad 10.$$

$$(\Delta H^\circ_{pep})_{obs} = \Delta H^\circ_{pep} - \sum \frac{K_{ij}}{K_{ij} + 1} \Delta H^\circ_{ij} \qquad 11.$$

$$(\Delta S^\circ_{pep})_{obs} = \Delta S^\circ_{pep} - R \sum \ln (K_{ij} + 1) - \frac{1}{T} \sum \frac{K_{ij}}{K_{ij} + 1} \Delta H^\circ_{ij} \qquad 12.$$

These equations apply to heterologous single bonds between nonionizable donors and acceptors, and the summations are taken over all such bonds. Other expressions are available for other types of hydrogen bonds (96, 97). From equations 10, 11, and 12, estimates have been made of the number of side-chain hydrogen bonds required to make $(K_{pep})_{obs}$ significantly less than $K_{pep}$. In a particular case (97), about 10 heterologous single bonds or, alternatively, one or two homologous double bonds would be sufficient to make the hydrolytic reaction appear to be a reversible one. This reversibility has been observed in the thrombin-fibrinogen reaction (93, 151) in which the liberated peptide is quite large, and in which carboxyl-carboxyl double hydrogen bonds may be involved. Reversibility may also be present in the pep-

sinogen-pepsin reaction (68, 69). However, it has not been observed in other zymogen-activation reactions, presumably because the liberated peptides are too small to have the required number of hydrogen bonds to the protein core.

*Protein association.*—Protein associations or polymerizations may also involve side-chain hydrogen bonds. As an example of such a reaction, we shall discuss the association of fibrin monomers to form intermediate polymers (24, 151). Thermodynamic studies of pH (36, 113) and enthalpy (176) changes accompanying association have led to an identification (176) of the donor and acceptor groups in this particular case (36, 176). The association is assumed to involve intermolecular hydrogen bond formation between $s$ donors on one molecule and $s$ acceptors on another molecule. Since both the donors and acceptors can ionize, the extent of hydrogen bond formation is pH-dependent. Each of the donors and acceptors is assumed to be involved in equilibria of the type (36, 150, 176)

$$DH \rightleftharpoons H^+ + D^- \qquad 13.$$

$$AH^+ \rightleftharpoons H^+ + A \qquad 14.$$

$$DH + A \rightleftharpoons DH \cdots A \qquad 15.$$

Formation of a hydrogen bond between a given $i^{th}$ donor and $j^{th}$ acceptor, according to equation 15, disturbs the acid-base equilibria of equations 13 and 14. Hence, at the low-pH end of the range of polymerization, protons will be produced because of the polymerization-induced dissociation of $AH^+$, whereas protons will be taken up at the high-pH end of the polymerization range when the polymerization causes $D^-$ groups to combine with hydrogen ions.

Quantitative studies (36, 176) of the equilibria involved indicate that there are about $s = 19$ histidyl acceptors and 19 donor groups (probably tyrosyl residues) between which hydrogen bonds can form. The donors and acceptors have been identified by their p$K$'s and heats of ionization. The actual number of hydrogen bonds formed between these groups is pH-dependent, with a maximum number of about 10 being formed around neutral pH. The number of hydrogen bonds drops to zero below about pH 5 (where the histidyl groups acquire protons and can no longer function as acceptors) and above approximately pH 10.5 (where the tyrosyl groups lose their protons and can no longer function as donors). Thus, the model accounts for the observed range, approximately pH 5 to 10.5, in which polymerization takes place, for the pH changes occurring during polymerization, as well as for the observed pH-dependence of the heat of polymerization.

The formation of antigen-antibody complexes also involves reactions between the side chains, and thermodynamic studies have been carried out on these association reactions (4, 126, 172). The thermodynamics of a variety of other protein association reactions, involving side-chain groups, have been carried out by Steiner (165 to 173). An extensive review of the problem of protein-protein association has been presented by Waugh (193).

*Kinetics of protein denaturation.*—For years it has been recognized that protein denaturation involves the rupture of hydrogen bonds. The pH-dependence of the rate of denaturation can be explained in terms of the rupture of tertiary hydrogen bonds, whereas the thermodynamics for the over-all reaction, in which native protein is converted to denatured protein, seems to involve, in addition, a disruption of the secondary structure (e.g., a helix-random coil transformation).

An early successful quantitative theory of the kinetics of protein denaturation was that of Steinhardt (174), extended by Levy & Benaglia (103). This theory considers that the protein can exist in many ionic forms depending on the pH, and that the stability of these may vary. A more recent theory (94) retains these postulates but introduces explicitly the effect of side-chain hydrogen bonding (in terms of $K_{ij}$). From the effect of $K_{ij}$ on the ionization constants and from the dependence of the rate on pH it is possible to identify the groups involved. Also, the explicit introduction of hydrogen bonding permits treatment of complex types of hydrogen bonding situations. Thus, in cases where the older theory (103, 174) cannot account for complex dependences on hydrogen ion concentration, the new theory can (94).

In the newer theory (94), the same model is used as in the derivation of equations 7 to 12. The transition state theory is used to treat the equilibrium between a native protein (based on this model) and the activated complex which differs from the native protein only in that some critical number of side-chain hydrogen bonds are simultaneously broken. It is assumed that no disruption of the helix takes place in the activation process. On this basis, it is possible to derive the following expressions which characterize the rate of denaturation when the activation process involves the rupture of $n$ equivalent heterologous single hydrogen bonds at a pH where the donors and acceptors do not ionize.

$$\Delta F^{\ddagger} = nRT \ln (K_{ij} + 1) \qquad 16.$$

$$\Delta H^{\ddagger} = -\frac{nK_{ij}}{K_{ij} + 1} \Delta H^{\circ}_{ij} \qquad 17.$$

$$\Delta S^{\ddagger} = -nR \ln (K_{ij} + 1) - \frac{nK_{ij}}{K_{ij} + 1} \frac{\Delta H^{\circ}_{ij}}{T} \qquad 18.$$

The similarity between these equations and equations 7 to 12 is immediately apparent and, of course, exists because the same phenomenon (i.e., rupture of specific side-chain hydrogen bonds) appears in each type of reaction.

If the pH is varied and account is taken of the ionization of the donor and acceptor groups, the reaction rate constant $k$ will be dependent not only on temperature but also on pH. In such a situation expressions have been given (94) for $d \ln k/d\text{pH}$ for a variety of hydrogen bonding situations. These equations may be applied to experimental rate data to determine the

nature of the specific side-chain hydrogen bonds which contribute to the stabilization of the helical configurations of the native protein.

We can estimate this stability for the simple case covered by equation 16. For the rupture of one such heterologous single bond, there is a free energy change of $RT\ln(K_{ij}+1)$ or about 0.5 to 1 kcal., depending on the magnitude of $K_{ij}$. For homologous double bonds, this can amount to as much as 3 kcal. per double bond. Thus, a helix can acquire this much additional stabilization for every such side-chain hydrogen bond which exists. If, in addition, the protein is at a pH where the donors and acceptors can ionize, then the fraction of the molecules having such hydrogen bonds will be pH-dependent (94). Thus, the stability of the helix will vary with pH.

If protein denaturation involves the rupture of hydrogen bonds then the substitution of deuterium for hydrogen should lead to an isotopic effect on the rate of denaturation. Shugar & co-workers have carried out experiments on the kinetics of heat denaturation of proteins in $H_2O$ and in $D_2O$ (52, 53, 160, 161). The proteins considered were lysozyme, ribonuclease, and deoxyribonuclease. The rate measured was really the rate of enzyme inactivation. The isotope effect for inactivation ($k_H/k_D$) was found to be related to the activation energy and to decrease to approximately unity for low activation energies. Shugar & co-workers interpret the low activation energies and values of $k_H/k_D$ near unity as indicating that hydrogen bonding is not of great importance for enzymatic activity in those cases, i.e., hydrogen bonds may exist but the enzyme can be inactivated without rupturing a significant number of them. When the activation energy is large and $k_H/k_D$ becomes as large as five in one case, it is concluded that such inactivation involves the rupture of a considerable number of hydrogen bonds.

*Thermodynamics of reversible denaturation.*—In order to treat the thermodynamics for the over-all denaturation reaction, i.e., for the equilibrium between the native and denatured states, it is necessary to have a model for the transition from the activated state (described above) to the denatured state. It is possible to assume that the helices are preserved in the denatured state but that their positions relative to each other are different from that in the native state [e.g., by virtue of rotations about S—S bonds or by formation of side-chain hydrogen bonds which did not exist in the native protein (95)]. Another possible assumption is that the helices in the activated state have been rendered unstable because of the rupture of the $n$ critical tertiary hydrogen bonds and, therefore, that the transition from the activated to the denatured state involves a helix-random coil transition. The latter assumption is the one adopted in a recent theory (149) for the equilibrium between native and denatured protein. This theory thus combines the thermodynamics of the activation process (94) with that for the helix-random coil transition (43), i.e., the free energy change for the over-all reaction is the sum of the free energy changes for the transformations from native to activated, and from activated to denatured states, respectively. The

pH dependence of the equilibrium constant is assumed (149) to arise solely from the activation step, since it is only during activation that the ionizable side-chains play a role. The relative magnitude of the pH-dependence provides a measure of the helical content. For example, a perfect helix would be less influenced by a side-chain hydrogen bond than would be an imperfect one of marginal stability. Further, whereas simple electrostatic theories based on the Linderstrøm-Lang model require symmetry about the isoelectric point, with maximum stability of the protein occurring at the isoelectric point, the hydrogen-bond theory indicates that the pH (or pH's) of maximum stability occurs in a region which depends on the p$K$'s of the donor and acceptor groups involved and needs bear no relationship to the isoelectric point. As yet, no quantitative data are available to test the theory. However, qualitatively, the pH behavior predicted for a number of hydrogen bonding situations seems to be similar to that found by Terminiello, Bier & Nord (186) in the reversible denaturation of trypsin, acetyltrypsin, and succinyltrypsin. The equilibrium theory offers the possibility of determining the side-chain groups which are important in reversible denaturation.

According to the theory presented above, rupture of hydrogen bonds (as, for example, in denaturation) may, in an appropriate pH range, lead to association or dissociation of protons, since the p$K$'s change when the hydrogen bonds are ruptured (e.g., see equation 7). Such effects have been observed by Harrington (61) in the case of ovalbumin, where protons are taken up at low pH and liberated at high pH, and by Edelhoch (34) in the case of pepsin, where protons are liberated, when the proteins are denatured by guanidine hydrochloride and by high pH, respectively. While Harrington and Edelhoch attribute their results to the rupture of tertiary hydrogen bonds, a view in which this writer concurs, it must be pointed out that p$K$'s can also be changed by alterations in electrostatic interactions during denaturation.

This same theory (149), applied to reversible denaturation in solution, has also been used to treat the pH dependence of the elastic properties of protein fibers. As in the Flory theory (43), the elastic properties are assumed to reflect the helix-random coil transition. The pH-dependence arises because the existence of the side-chain hydrogen bonds (and their influence on the stability of the helices) depends on the pH. Thus, $\Delta h'$ of equation 2 contains an additive pH-dependent contribution from the rupture of the side-chain hydrogen bonds. Calculations of the effect of the side chains on the $f$-$T$ curves leads to a pH-dependent transition temperature (at a given force) which varies according to the type of side-chain hydrogen bonding assumed. Some of the calculated curves are very similar to those observed, e.g., for the pH-dependence of the shrinkage of collagen (101). Further studies on the pH-dependence of the elastic properties of protein fibers should shed light on the tertiary structure.

### Location of Specific Tertiary Hydrogen Bonds

Considering the important role which the tertiary hydrogen bonds appear to play, not only in the stability of the secondary structure, but also in so

many different types of protein reactions, it is worthwhile to consider some experiments designed to locate specific side-chain hydrogen bonds.

As a first example, we may cite the use of titration data. On the basis of the abnormality of the p$K$'s of tyrosyl and carboxyl groups, Tanford & Roberts (177, 178, 185) suggested the possible existence of a tyrosyl-carboxylate ion hydrogen bond in serum albumin. A quantitative consideration (96, 110) of the thermodynamic parameters for the ionization of the groups involved in this bond in serum albumin has led to the evaluation of the corresponding thermodynamic parameters for the formation of such a bond, as already discussed.

A recent attempt has been made (59) to determine whether the B-29 lysyl $\epsilon$-amino group of insulin is hydrogen bonded by examining its ionization properties. Iodinated insulin was used to shift the region of tyrosyl ionization away from that of the ionization of the lysyl amino group. It should be recalled that insulin contains only one lysyl residue (135) so that this study provided information on the ionization of a single group without having to consider statistical factors. The p$K$ and $\Delta H$ were found to be normal, i.e., $\Delta F^\circ_{obs}$, $\Delta H^\circ_{obs}$, and $\Delta S^\circ_{obs}$ of equations 7, 8, and 9 did not differ appreciably from $\Delta F^\circ_1$, $\Delta H^\circ_1$, and $\Delta S^\circ_1$, respectively. Hence, the B-29 lysyl amino group does not appear to be involved in a hydrogen bond. Had such a bond existed, it would presumably have been detected in this study, and the further identification of the acceptor group would have given knowledge, not only about a specific tertiary hydrogen bond but also information on the secondary folding of the backbone chain.

Another study in which the ionization of a single group was involved was that of Klotz & Ayers (85). Their study was made on a dimethylamino group of a dye bound to the SH group of bovine serum albumin, rather than of a naturally occurring ionizable side-chain group. The p$K$ of the dimethylamino group was 3.3 and 1.8 when the dye was bound to cysteine and to bovine serum albumin, respectively. Klotz & Ayers suggested that the lower p$K$ in the protein was not due to electrostatic effects. They attribute the lower p$K$ to a change in the water structure around the protein as the albumin goes through its well-known structural change (201) at low pH.

Specific tertiary hydrogen bonds may also be detected in studies of the effect of pH and enzymes on ultraviolet difference spectra arising from hydrogen bonded tyrosyl residues in proteins. Such experiments have been reported for insulin (98, 99) and ribonuclease (148, 157) and were interpreted as implicating the tyrosyl residue(s) as a donor to a carboxylate ion acceptor. For ribonuclease this conclusion is compatible with the abnormal behavior of three of the six tyrosyl residues (9, 159, 163, 183). Ultimate location of the specific tyrosyl groups which may be hydrogen bonded will provide another restriction on the secondary structure. In bovine serum albumin (196) the rupture of tyrosine hydrogen bonds, as detected by difference spectra, results from the general structural change which occurs at low pH (201). The acceptors of the tyrosine hydrogen bonds in serum albumin remain unidentified. Intermolecular tyrosyl-carboxylate ion hydrogen bonds in model com-

pounds have also been detected by the spectrophotometric method[3] (91, 194). However, electrostatic effects can also give rise to similar spectral changes (5, 17, 25, 26, 51, 156, 195) in compounds in which tyrosyl hydrogen bonds cannot exist. There is not yet a quantitative evaluation of the relative contributions which can be made by hydrogen bonding and by the electrostatic effect. Presumably both effects can contribute and care must be taken in the interpretation in a given case. This general problem has recently been discussed by Laskowski (92). In lysozyme the effect appears to be an electrostatic one arising from ionizations of carboxyl groups near tryptophan residues (25, 26). From the difference spectra, it has been possible to identify two kinds of carboxyl groups by their apparent p$K$'s (3.2 and 6.1). These values are in reasonably good agreement with the intrinsic p$K$'s of 3.5 and 5.1 determined from direct titration data of lysozyme (7) with the electrostatic factor of equation 5 being obtained from the electrokinetic potential (from electrophoresis experiments).

As indicated earlier, it is difficult to decide whether an abnormal p$K$ is due to local electrostatic effects or to specific hydrogen bonding of the dissociable groups. This is essentially one of the disadvantages of the use of titration data for locating internal hydrogen bonds. Also, titration curves provide no information on hydrogen bonds involving nonionizable groups such as serine. However, if one considers the titration data together with other information (e.g., ultraviolet difference spectra, modified reactivity of peptide bonds in limited proteolysis, pH-dependence of the rate constants and equilibrium constants in denaturation, behavior of protein derivatives, etc.), it may be possible to distinguish between hydrogen bonding and local electrostatic effects.

Limitations of space prevent discussion of numerous other experiments indicating the presence of specific tertiary hydrogen bonds in proteins.

## Disulfide Bonds

Before concluding, it is of interest to emphasize the important contribution which disulfide bonds make to the tertiary structure. As pointed out by Schellman (143) and Flory (43), the disulfide cross-link imposed on a helical configuration provides considerable additional stability for the helix. When these disulfide bonds are broken by oxidation or reduction the resulting structures are less likely to be found in a helical configuration. Presumably, it is the rupture of the disulfide bonds, rather than the charge on the resulting sulfur group, which affects the stability. As examples, we may cite insulin and ribonuclease which have a certain amount of helical structure which is lost upon oxidation of the S—S bonds (63, 75, 76, 77, 100, 145, 158). On the other hand, the disulfide bonds of a native protein may actually constrain the protein to nonhelical configurations. Thus, in human serum albu-

[3] For a possible involvement of the peptide groups in hydrogen bonding, with resulting effects on the absorption spectrum, see Schauenstein (142).

min, Markus & Karush (80, 112) found that rupture of the disulfide bonds by reduction permits the reduced product to acquire a higher degree of secondary structural folding than exists in the native protein.

For an extensive review of this and related topics, see S. J. Leach, "The Configuration of Proteins in Solution," *Reviews of Pure and Applied Chemistry (Australia)*, **9**, No. 1 (1959).

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# HETEROGENEOUS EQUILIBRIA AND PHASE DIAGRAMS[1,2]

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The last chapter on Heterogeneous Equilibria and Phase Diagram for the *Annual Review of Physical Chemistry* appeared in 1956. In the three years following, numerous publications related to the subject of this review have appeared in the literature. It was evident that within the limits of space available to the reviewer an attempt to treat this amount of work in a comprehensive manner would not be realistic. It was therefore decided that a general survey of experimental work appearing in the period 1957–1958 would be made, although in a few instances references are made to work appearing in 1956. Regrettably it has, therefore, been necessary to omit a few of the sections which have usually been covered by previous authors. It is hoped that future authors of this review will note this in preparing their articles. In sections dealing with phase relationships, the present review is concerned only with systems for which new or confirmatory phase data have been reported. No attempt has been made to discuss the large number of articles dealing with the various properties of systems where phase relationships have already been established.

*Determination of thermodynamic activities and phase boundaries.*—In the last few years, a great deal of experimental work has been directed toward measurements of thermodynamic properties of systems with two or more components. Thermodynamic quantities such as partial molar heats and entropies are useful for theoretical considerations in that they may provide information on the chemical bonding and the degree of order in these systems. Oriani (1) has recently reviewed the present day theories of bonding in primary metallic solutions. Partial molar free energies are generally obtained from measurements of thermodynamic activities for one component and use of the Gibbs-Duhem equation to calculate the activity for the second component. Entropies of mixing are frequently obtained from the temperature dependence of activities or by combination of calorimetric heats with free energy measurements. Kleppa (2) has computed entropies in this manner for a large number of binary metal alloys. Anderson (3) has summarized the experimental results of several independent determinations of activities in the $\alpha$-phase of the Ag-Cd system. Although fair agreement in values of $\Delta\overline{F}_{Cd}$ for various alloy compositions were obtained in these studies, the integral heats of formation for alloys computed from measurements of activity as a function of temperature did not agree in some cases with values

[1] The survey of literature was completed December, 1958.

[2] The following abbreviations will be used: B.C.C. (body centered cubic); DTA (differential thermal analysis); E.M.F. (electromotive force); F.C.C. (face centered cubic); and HCP (hexagonal close packed).

obtained by the direct calorimetric method. This emphasizes the importance of having an independent check on heats obtained by indirect methods.

Wagner (4) has developed a method for obtaining approximate values of free energies of formation of binary compounds with the aid of phase diagram data and heats of fusion. Schottky & Bever (5) have applied this method to the calculation of the free energies of formation of the compounds InSb and GaSb.

The methods most generally used for measurements of thermodynamic activities were E.M.F., vapor pressure, and gas phase reaction. These methods are also employed in determining phase boundaries in the composition diagram. Other methods commonly used for the latter purpose were x-ray, conventional thermal analysis, differential thermal analysis, quenching, microscopic examination, electron and neutron diffraction techniques, and changes in physical properties (i.e., electrical resistance, etc.).

*E.M.F. measurements.*—E.M.F. methods have been used quite frequently for activity measurements in binary metal systems; generally the potential difference between the alloy and one of the pure components is measured as, for example, in the (Al)-(Al, Ag) couple (6). Some of the problems involved with measurements on liquid Cu-Ag alloys have been discussed by Edwards, Downing & Cubicciotti (7). The selection of an adequate electrolyte for E.M.F. measurements on metal systems presents a formidable problem. To be used satisfactorily, the electrolyte must not undergo displacement reactions with the electrodes and must not show electronic conduction. If the alloys are liquid, there is also the possible danger of their reaction with the cell containers. Bohl & Hildebrandt (8) have made electrode potential measurements on liquid Zn-Cd and Zn-In alloys, which also provide information on the liquidus curves. Panish *et al.* (9) used a molten electrolyte consisting of a mixture of NaCl, RbCl, and a small amount of $CrCl_2$ for measurements of Cr activity in Cr-Ni alloys with compositions extending to the two phase region. Their results are compared with Cr activities obtained by earlier workers from studies of the equilibrium involving $H_2O(g)$, alloy, $H_2(g)$, and $Cr_2O_3(s)$. Verduch & Wagner (10) have discussed the use of solid AgI electrolyte for E.M.F. measurements in the (Ag)-(Ag, Sb) couple. Heats of mixing of Au-Cu, Ag-Cu, and Ag-Au alloys obtained by E.M.F. methods have been compared by Oriani & Murphy (11) with values obtained calorimetrically.

Stern (12) and Panish *et al.* (13) have measured activities of AgCl in liquid AgCl-NaCl solutions with use of the cell Ag/AgCl, molten NaCl /$Cl_2(g)$, graphite, for temperatures extending to above 900°C. Activities are obtained relative to the standard cell with zero mole fraction of NaCl. Panish's measurements for the standard cell extend to about 800°C. while Stern's go to about 650°C. The experimental arrangement used by both investigations is very similar although Stern used Vycor cells while Panish used fused silica vessels. In Panish's work, the entire surface of the molten electrolyte is under an atmosphere of $Cl_2$ gas. The two sets of data are in

substantial agreement for high concentrations of AgCl but deviate somewhat at low concentrations of AgCl. Panish & co-workers have also measured activities in solid AgCl-NaCl solutions and find an unusual shape in the activity versus composition curve, which is indicative of a miscibility gap.

Some of the more subtle aspects concerning contact potentials and their significance in electrochemical measurements is the subject of an interesting article by Bjerrum (14).

Aronson & Belle (15) have made a thermodynamic study of the U-O system in the nonstoichiometric phase region $UO_2$-$UO_{2.2}$ at temperatures between 1150°–1350°K. The electrochemical technique developed by Kiukkola & Wagner (16) was used. Cells of the type Fe, $F_{0.95}O$ ($ZrO_2$+CaO) $UO_{2+x}$, Pt were used to measure the activities of $O_2$ in the $UO_{2+x}$ phases. The over-all cell reaction may be represented 1.9 Fe+$O_2$ (in $UO_{2+x}$) = 2 $Fe_{0.95}O$. Their measurements extend to the composition range above $UO_{2.2}$ where a break in the E.M.F. curve corresponds to a two phase region presumably $UO_{2+x}$ and $U_4O_{9-z}$.

*Vapor pressure techniques.*—In the vapor pressure methods, the activity of a component in the condensed phase is determined from measurements of the partial pressure of gaseous species relative to that for the pure liquid or solid phase. This type of measurement involves the assumption that (*a*) true vapor-condensed phase equilibrium is attained and that (*b*) the composition of the vapor phase is known. In recent years, mass spectrometers have been used quite frequently for obtaining information on the composition of vapors, The vapors in many metal systems (17, 18), for example, have been studied this way. The vapor phases in many salt systems are known to contain large concentrations of polymeric species. Molecular beam (19, 20) and mass spectrometric studies (21, 22, 23) of alkali halides show the presence of monomers, dimers, and, in some systems, trimers in the vapor phase. Systems such as NaF-LiF (23) also contain mixed dimers, $NaLiF_2$, in addition to dimers of NaF and LiF. One would speculate that the gas phase in the LiF-NaCl systems would contain no less than 13 monomer and dimer species. Beusman (24, 25) has made an extensive investigation of activities in the KCl-$FeCl_2$ and LiCl-$FeCl_2$ systems. He has taken into account, the presence of dimers in the vapor phase by using both static (i.e., total pressure) and transpiration methods for measuring pressures. Consistency between the results from the two methods is obtained only if corrections for dimers are made. The problem is more complicated for the LiCl-$FeCl_2$ system since there is a significant concentration of LiCl trimer in this system. For pure $FeCl_2$, Beusman's measurements indicate about 20 per cent dimer in the vapor in equilibrium with the liquid phase. Extrapolation of data obtained from mass spectrometric studies on the vapor phase of solid $FeCl_2$ also indicate dimer concentrations of this magnitude in the vapor above the liquid. Beusman's measurements extend over a large composition and temperature range and give evidence for the existence of a gaseous complex, $KFeCl_3$, in the vapor. Using a dew point technique, Howell, Som-

mers & Kellogg (26) have measured vapor pressures of $ZrCl_4(g)$ in the $NaCl\text{-}ZrCl_4$ and $KCl\text{-}ZrCl_4$ systems. In their temperature range, the vapor pressure of alkali halide is small. Their pressure measurements extend over a large composition range in the $NaCl\text{-}ZrCl_4$ system and define the homogeneous region in the composition diagram. Their measurements also show a pressure plateau in the central region of the diagram corresponding to the two phase, solid-liquid region. Cantor & co-workers (27) determined activities in the $RbF\text{-}ZrF_4$ system from measurements of the $ZrF_4$ pressure by the use of a differential monometer (i.e., quasi-static method). For activity determinations in solutions of $Bi\text{-}BiBr_3$, Cubicciotti & Keneshea (28) employed transpiration techniques to measure the vapor pressure of $BiBr_3$. Analysis of transported material shows that the composition of the vapor on equilibrium with $Bi\text{-}BiBr_3$ mixtures is close to $BiBr_3$.

Edwards & Downing (29) used the Knudsen effusion technique to determine activities in the Ag-Cu system. This method is applicable to systems at temperatures where the vapor pressure is usually between about $10^{-8}$ and $10^{-4}$ atm. The pressure of gas is low enough so as to obey molecular flow. The rate of gas effusion from a small orifice in the cell is determined by noting the weight of material that leaves the cell in a specified amount of time. This, in turn, is used in the kinetic equation for gases to compute the pressure of gas within the cell. A small orifice is used to help insure that total vapor saturation is attained in the cell. Edwards & Downing determined both the Cu and Ag content of the vaporized material and could thus calculate activities of both components directly. McCabe, Hudson & Paxton (30) used the effusion method to determine activities in Fe-Cr alloys at 1205 and 1250°C. Their results indicate nearly ideal solution behavior. Nesmeyanov, Smakhtin & Lededev (31) also used this method for vapor pressure measurement on Au-Ag and Au-Cu solutions, but modified the method by labeling the three metals with radioactive isotopes for analytical purposes.

Blackburn (32) has obtained thermochemical data for the U-O system from measurements of the dissociation pressure of oxygen from uranium oxides. His Knudsen cell was suspended on a microbalance permitting continuous pressure measurements as the oxygen content in the condensed phase changed. The measurements extend from solid compositions $UO_{2.0}$ to $UO_{2.6}$ in the temperature range 950–1150°C. Plateaus in the $log\ P_{O_2}$ versus the atomic ratio of O to U are observed corresponding to the two-phase regions $UO_{2+x}\text{-}U_4O_{9-y}$ and $U_4O_{9-y}\text{-}U_3O_{13}$. A portion of the phase diagram over the composition range studied is given. The homogeneity range for $UO_2$ is much larger than for $U_4O_9$.

Flow methods have also been used recently for pressure measurements in alloy systems. In this method, a circulating, nonreactive gas is passed over the alloy of known composition and the vapor pressure (usually of the more volatile component) is determined from the volume of gas and the weight of material transported. This technique was used by Everett, Jacobs & Kitchener (33) and by Morris & Zellars (34) to measure vapor pressures

of Zn and Cu in Zn-Cu and Cu-Fe alloys, respectively. In both the effusion and flow methods, the amount of material transported is generally small so as not to affect the bulk composition of the alloy.

Herasymenko (35) studied Ag-Cd alloys formed by the reaction of solid Ag with Cd vapor. His apparatus consisted of a closed, evacuated tube containing at one end liquid cadmium, and at the other end, Ag wires. The cadmium was heated to a desired temperature for which the vapor pressure is accurately known. The vapor circulates throughout the tube and reacts with the Ag wires which are heated to a temperature higher than the cadmium but in such a way that successive wires are in a temperature gradient. When the Cd has equilibrated with the Ag, the resulting alloys are analyzed for composition. The activity of Cd in each specimen is then determined from the temperature-vapor pressure curve for pure cadmium. With this method, a large number of activity measurements may be obtained in one experiment. The method seems to suffer somewhat from the fact that the rate of attaining equilibrium may be slow, depending on the rate at which the metals diffuse into the alloy. Scatchard & Boyd (36) measured vapor pressures of Cd in Ag-Cd alloys by an interesting spectrophotometric technique involving the absorption of an intense Cd resonance line by the Cd vapor. Rosenthal, Mills & Dunkerley (37) used a method similar to Herasymenko's to determine activities in Pb-Zn alloys between 600° and 900°C. In their experiments, Zn vapor is equilibrated with Pb samples which contain some Zn initially. They also obtained activities in the range 400° to 650°C. from E.M.F. measurements. The two sets of data at 600°C. are in good agreement. The higher temperature measurements help to define the phase boundary for the liquid miscibility gap. Rayson & Alexander (38) used an isopiestic technique to determine the phase boundaries in the Ag-Cd and Cu-Cd systems. In their method, samples of silver and copper are simultaneously equilibrated with cadmium vapor at a value fixed by the temperature of pure condensed Cd. The cadmium alloys formed are then analyzed and a plot of percentage weight composition for one is plotted against that for the other. Breaks in the curves correspond to phase boundaries at composition indicated in the axes. Predel (39) determined activities of Cd in Ga-Cd alloys by equilibrating Cd vapor from Sn-Cd alloys with Ga metal under the same experimental conditions. The activity of Cd in the final Sn-Cd alloy is known and the activity of Cd in the Ga-Cd alloy is, therefore, obtained. Orr, Goldberg & Hultgren (40) have compared their calorimetric values for the heats of formation of Ag-Cd alloys with values obtained from vapor pressure measurements. The thermodynamic properties (i.e., $\Delta\overline{F}$, $\Delta\overline{H}$, etc.) for Ag-Au alloys over a wide composition range have been tabulated by White, Orr & Hultgren (41).

Using a manometric technique, Westrum & Machol (42) measured the dissociation pressures of tellurium from liquid and solid nickel telluride. For pressure measurements, they used a Bourdon type gauge in which the pressure of hot tellurium vapor on one side of a thin piece of silica is balanced on

the other by the pressure of an inert gas. The pressure of the inert gas is then measured in a conventional manometer. They obtained vapor pressures of solid solutions with compositions $NiTe_{1.5}$, $NiTe_{1.9}$, and $NiTe_{2.0}$ as a function of temperature. Isothermal plots of pressure versus composition shows a plateau corresponding to the solid-liquid region. Pressures of alloys with composition $NiTe_{2.0}$ and $NiTe_9$ coincide at temperatures below 682°C. showing that $NiTe_{2.0}$ coexists with the liquid. Tellurium activities were determined relative to molecular $Te_2$ since this form is believed to exist in the vapor phase.

In systems where one component is normally a gas (i.e., Ti-$H_2$ system) (43) static methods for pressure measurements are usually employed. Frequently the equilibrium is approached from the gas side. Libowitz, Hays & Gibb (44) obtained pressure-composition isotherms for the Zr-Ni-$H_2$ system and found a Pressure plateau indicating a two phase region bounded by a $ZrNiH_3$ phase and a phase of the probable composition ZrNiH. The Nb-$H_2$ (45) system has been studied at pressures from 10 to 1000 mm. of Hg and temperatures between 100° and 900°C. Solid solution behavior is observed with H to Nb ratios from .01 to .85.

*Gas-condensed phase reactions.*—Thermodynamic activities for components in condensed phases have been obtained from studies of the equilibrium between a reactant gas, condensed phase and product gas. This method is applicable to systems for which the two methods mentioned previously are generally not feasible. It has been used frequently for determination of sulphur and oxygen activities. The method is also used to obtain information on phase boundaries in heterogeneous systems. Chipman (46) has recently discussed the theory and experimental methods and has reviewed some of the early literature.

Floridis & Chipman (47) investigated the reaction $H_2(g)+O$ (dissolved in Fe alloys) $= H_2O(g)$. When the system is at equilibrium, the activity of oxygen in the condensed phase is proportional to $P_{H_2O}/P_{H_2}$. In these experiments, a mixture of predetermined composition of $H_2O$, $H_2$, and argon is equilibrated with liquid iron alloys and the final oxygen content in the condensed phase is determined analytically. Their results include the effect on the activity coefficients of oxygen due to varying amounts of the second metal component. They also discuss their present results in light of earlier work on the Fe-O system in which $H_2O$-$H_2$ and $CO_2$-CO mixtures were used.

Verduch & Wagner (10) have discussed thermodynamic data based on the reduction of sulphides with hydrogen. Continuous reaction of quasi binary systems as PbS-$Sb_2S_3$ and $Cu_2S$-$Sb_2S_3$ with $H_2(g)$ to form $H_2S(g)$ depletes the condensed system of sulphur and thus serves to vary the over-all composition with the subsequent formation of new condensed phases in proceeding across the composition diagram. The equilibrium quantity $P_{H_2S}/P_{H_2}$ is a measure of the sulphur activity for a given composition. Plateaus in the quantity are observed as the composition varies, showing the regions in which double salts exist. Rivsky & Schuhmann (48) determined thermodynamic

data for the Cu-Fe-S system in the temperature range 1150°–1350° from measurements of $P_{H_2S}/P_{H_2}$. These ratios were obtained as a function of composition and correspond to regions of one, two, or three condensed phases. Alcock & Richardson (49) determined activity coefficients of sulphur in binary Cu alloys containing Au, Si, Pt, Co, Fe, or Ni at temperatures between 1100°C. and 1500°C. In these experiments, $H_2S$-$H_2$ mixtures were equilibrated with beads of pure copper and of copper alloys under the same experimental conditions. The distribution ratio of sulphur between pure copper and alloy was obtained for a wide range of alloy compositions at several temperatures. Alcock (50) has used $H_2S$-$H_2$ mixtures in which sulphur is labeled with radiosulphur $S^{35}$. This allows for rapid analysis of the equilibrium gas by counting techniques. The method also provides good sensitivity. His measurements with $H_2S$-$H_2$ mixtures for the Fe-S, Co-S, and CuS systems are in good agreement with those obtained in early studies of these systems with conventional methods.

Turkdogen, Leake & Masson (51) measured carbon activities in iron-carbon melts by following the reaction $C(\text{dissolved in iron}) + 2H_2(g) = CH_4(g)$. The equilibrium quantity $P_{CH_4}/P_{H_2}^2$ is proportional to the carbon activity (relative to $\beta$-graphite) and was measured as a function of carbon content. Their results are compared with those of an earlier study involving the reaction $C(\text{dissolved in Fe}) + CO_2(g) = 2CO(g)$, after the latter results are corrected for the amount of dissolved oxygen. Cordier (52) has pointed out that in this type of experiment the presence of CO in the system due to reaction of carbon with CaO in ceramic containers may lead to high results, because of the side reaction $CO + 3H_2 = CH_4 + H_2O$.

*Binary metal systems.*—Because of the appearance of a large number of papers dealing with metal systems, the following sections will necessarily be limited to a brief account of individual systems. The publication of *Constitution of Binary Alloys* (53) in the Metallurgy and Metallurgical Engineering Series in 1958 will be of invaluable aid to the metallurgist and the physical chemist. This comprehensive volume compiled by Hansen with the cooperation of Anderko contains nearly 10,000 references, some of which are as late as 1957. The work includes 1334 binary systems and 717 phase diagrams not including additional material inserted in proofs. The diagrams are given linearly in atomic per cent composition.

Messer & co-workers (54) studied solid-liquid equilibria in the Li-LiH system from 13 to 99.8 mole per cent LiH with thermal analysis techniques. Their results indicate a monotectic point in the system at 685°C.; Salmon & Ahmann (55) used thermal analysis to investigate the two-phase liquid region in the Li-Na system. Results of their study give an estimated critical temperature of 380°C. In a series of x-ray investigations on the solid phases in the Li-Pb system, Zalkin & Ramsey (56) determined lattice parameters for five intermetallic compounds, LiPb, $Li_3Pb_3$, $Li_3Pb$, $Li_7Pb_2$, and $Li_{22}Pb$. In many cases, these phase compositions differ from those reported in earlier work on this system. Similar studies on the Na-Pb system have been carried

out by Weston & Shoemaker (57). Keller, Kanda & King (58) used thermal analysis to determine the liquidus and solidus curves in the Li-Ba system. Their results show that the compound $BaLi_4$ melts incongruently at 150°C. They also found no measurable solid solubility. Krier & co-workers (59) determined the incongruent melting point of $Na_2K$ and the $Na_2K$-K eutectic temperature. These results are in essential agreement with the phase diagram given by MacDonald, Pearson & Towle (60) who measured changes in electrical resistance to fix the liquid-solid phase boundaries.

Because of disagreement in earlier measurements on the Mg-Ba liquidus curves for Ba composition above ten per cent, Anderko (61) has redetermined this portion of the phase diagram. These results support the early work of Klemm & Dinkelacker (62). The portion of the Mg-Zn diagram from 0 to 85 weight per cent Zn has been reinvestigated by Clark & Rhines (63). They report four solid phases, $Mg_7Zn_3$, MgZn, $Mg_2Zn_3$, and MgZn. The phase $Mg_2Zn_3$ has not appeared in some of the earlier versions of the Mg-Zn diagram (see Hansen, p. 927). An x-ray study of the Mg-Cd system from 22 to 50 atomic per cent Cd has been made by Moore & Raynor (64). These results indicate the ordering of two super lattices of MgCd and $Mg_3Cd$. Clark & Rhines (65) have studied the Mg-Al system by observing the diffusion layers formed between pure Al and Mg. From their studies the existence of only three stable intermetallic compounds in the system is indicated. Anderko, Yamamoto & Rostoker (66) have determined the solubility of Fe in Mg by comparing the total iron content for two coexisting Fe and Mg phases obtained by chemical analysis, with that obtained by magnetic analysis, which gives only the amount of undissolved Fe. Horsley & Maskrey (67) studied a small portion of the Mg-Pb system from 0 to 3 weight per cent Mg and report an eutectic at 248.5°C. Hirst, King & Kanda (68) using thermal analysis, obtained liquidus and solidus curves for the Ba-Sr system over the complete range of composition. They also studied the solid phases by means of x-ray diffraction. The system is found to resemble the Ca-Ba system in many respects. Complete miscibility in the liquid phase is observed and the components form a continuous series of solid solutions. In the solid region at high Sr content, an eutectoidal point is observed at which the H.C.P. (Hexagonal Close Packed) structure is in equilibrium with the F.C.C. and B.C.C. forms. The Ca-Sr (69) system has also been studied over the entire composition range by differential thermal analysis. Liquidus and solidus curves were obtained. Complete miscibility in both liquid and solid ranges is observed. The system is of interest because the components undergo the same phase transitions for increasing temperature, F.C.C.→H.C.P.→B.C.C. Alloys exist in the same three crystalline modifications. The variation in lattice parameter as a function of composition is linear for the F.C.C. form in accordance with Vegard's law. A comprehensive review on the subject of lattice spacing relationships and the application of Vegard's law to alloy systems has been given by Massalski (70). The structures of a series of intermetallic com-

pounds (i.e., $CaPt_2$) of the alkaline earth metals (Ca, Sr, Ba) with noble metals (Rh, Pd, Ir, Pt) have been determined by x-ray diffraction (71).

The Al-Ga system has been studied by Clare (72) who used thermal analysis and by Zoller (73) who used thermal analysis and changes in electrical resistance to set the phase boundaries. The system exhibits a simple eutectic point at 26.6°C. No evidence was found by Clare for intermetallic compound formation.

A large amount of phase data for systems of transition metals have been reported in the last few years. Williams (74) has studied the Ni-Cr system and has measured terminal solid solubilities. There are points of disagreement of these results and earlier versions of the Ni-Cr diagram. As mentioned earlier, some work on this system has been reported recently by Panish *et al.* Nickel-copper alloys have been prepared by Hall & Alexander (75) through the reduction of a mixture of two metal oxides obtained from precipitated carbonates. A thorough mixing of the alloys results although the oxides are known to have different crystal structures. Williams (76) has investigated the miscibility gap in the Fe-Cr system. His studies involve the use of electrical resistance and neutron diffraction methods. Results of the neutron diffraction work are interpreted as disproving the existence of a $Cr_3Fe$ phase. Portions of the liquidus curves for Cr-Pb and Ni-Pb systems were determined by Alden, Stevenson & Wulff (77). The $\sigma$-phase in the Re-Cr, Ru-Cr, and Os-Cr systems has been investigated by x-ray diffraction by Waterstrat & Kasper (78). Phase transformation in Fe-Pt alloys near the composition $Fe_3Pt$ have been studied by Berkowitz & co-workers (79). An extensive x-ray study of the Fe-Al system from 0 to 62 atomic per cent Al has been made by Taylor & Jones (80). The work concerns the identification of intermetallic phases and measurements of lattice parameters. The Ti-Ce system was found by Taylor (81) to be of the peritectic type with no evidence for intermetallic compound formation between 0 and 50 per cent Ce. In the Ti-Sb system (82), a phase of composition $Ti_{2.5}Sb$ has been reported. It is structurally similar to $Ti_2Bi$. Through x-ray measurements Reidman & Averbach (83) examined the extent of ordering in Co-Pt solid solutions. Wood & co-workers (84) have determined lattice parameters for the intermetallic compounds $Nb_3Al$, $Nb_3Ga$, and $Cr_3Ga$. The structures are similar to $\beta$-Wolfram. These workers have also obtained more complete data for $Mo_3Ga$, $V_3Ga$, $V_3Sb$, and $Nb_3Sb$ from powder diffraction work. Bland & Clark (85) have made an x-ray examination of the $\epsilon$-phase in the W-Al system. The intermetallic compound $WAl_4$ is found to have monoclinic symmetry. Bland (86) has also studied the $\delta$-phase in the Mn-Al system and finds it to correspond to a compound $Mn_4Al_{11}$ with triclinic symmetry. Structural information from x-ray studies has also been obtained for the $\gamma'$-phase in the U-Mo system (87) and $\alpha$-phase in the V-Al system (88). The latter phase has composition limits from $VAl_{10}$ to $V_2Al_{21}$.

Blanchard & Cueilleron (89) give an extended diagram for the W-Si

system which includes the $WSi_2$ phase and a phase of composition $W_5Si_2$. This latter phase appears to correspond to the $W_3Si_2$ phase reported earlier. The variation in reported compositions is probably accounted for by the large homogeneity range. Further work on the Nb-Si (90) system has been reported with evidence for an $Nb_4Si$ phase in addition to $NbSi_2$ and $Nb_5Si_3$. Dauben, Templeton & Myers (91) have reported results of single crystal work on $Cr_5Si_3$ and find its structure similar to that of $Mo_5Si_3$ and $W_5Si_3$. X-ray studies (92) on $ZrGe_2$, $HfSi_2$, and $HfGe_2$ show these compounds to be isostructural. Notwotny, Searcy & Orr (93) made an x-ray study of some metal Germanides with the ideal composition $M_5Ge_3$. The compound with composition $NbGe_{0.54\pm.06}$ and the $\beta$-phase of $TaGe_{0.5}$ are structurally similar to $Mo_5Si_3$. The $\alpha$-phase of $TaGe_{0.5}$ is similar to the high temperature form of $Ta_5Si_3$. X-ray studies of the Th-Ge (94) system indicate the existence of at least six intermetallic compounds with compositions $ThGe_{3.0\pm0.4}$, $ThGe_2$, $ThGe_{1.6\pm0.3}$, ThGe, $Th_3Ge_2$, and $ThGe_{0.3\pm0.1}$. Similarities between $M_5Ge_3$ compounds with $M_5Si_3$ compounds have been shown by Parthé & Norton (95) from x-ray investigations. The compounds studied were $Zr_5Ge_3$, $Ta_5Ge_3$, and $Cr_5Ge_3$. Pell (96) has obtained information on the Li-Si system, including the eutectic temperature and the melting points of intermetallic compounds.

Two intermediate solid phases ($\beta$) and ($\gamma$), have been reported for the V-Te system (97). It is interesting that neither phase corresponds in composition to the simple mono or di-telluride. The $\beta$-phase lies close to the composition $V_5Te_4$ and appears to have no appreciable homogeneity range. The $\gamma$-phase, on the other hand, varies from about 53 to 65 atomic per cent Te, depending on the quenching procedure, and is found to exist in four crystalline modifications.

A portion of the Ag-Zr (98) diagram has been studied by Betterton & Easton. A phase with the composition $Zr_2Ag$ is reported. Further studies on the homogeneity range of this phase is, perhaps, needed since earlier work in the same composition range indicates a phase of composition near $Zr_3Ag$. Takahashi & Mihama (99) have used an electron microscope to study Cu-Al films vaporized on to NaCl surfaces. With this method, they are able to follow the transformation from $CuAl_2$ to CuAl, $Cu_9Al_4$, and $Cu_3Al$. Liquidus and solidus curves for the $\alpha$-solid solutions of Cd, In, Sn, and Sb in Ag and of Zn, Ga, Ge, and As in Cu have been discussed by Hume-Rothery & Burns (100). They have analyzed the liquidus curves and the lattice spacings in terms of empirical relationships. They have also given a diagram of the Cu-As system to about 50 atomic per cent As showing two intermetallic phases. Tiedema, Bouman & Burgess (101) used x-ray techniques to determine phase boundaries in the Au-Pt system.

Domagola, Elliott & Rostoker (102) have studied the Hg-Th system over the complete composition range to temperatures of 1000°C., with thermal, x-ray, and electrical methods. Two intermetallic phases HgTh and $Hg_3Th$ are reported. The HgTh phase decomposes eutectoidally between 400–500°C.

to $Hg_3Th$ and Th. Ferro (103) has also made an x-ray study of $Hg_3Th$. Lattice parameters for $Hg_3Th$ have been measured by both investigators. There is good agreement in the indexing of the compound. In the same paper, Ferro has also given lattice parameters for $ThIn_3$, $ThTl_3$, $ThSn_3$, and $ThPb_3$.

The increasing interests in the properties of semiconductors have resulted in phase studies of some of these materials. The liquidus curve for the InSb-InBi system (104) appears to run continuously from the melting point of InSb (525°C.) to the melting point of InBi (110°C.). If a eutectic exists, it is virtually indistinguishable from the melting point of InBi. The solid solubility of InBi in InSb is found to be less than .5 per cent at room temperature. Portions of the InSb-Sn system, which is of interest because Sn lies between In and Sb in the periodic table, has been investigated by Zitter (105). The InSb-liquid section was determined by heating and cooling curves. The work also includes some of the solid range. Work has also been reported on the In-Mg and In-Li systems (106). The In-Mg system is extended to about 60 atomic per cent Mg. The solid solubility of Mg in In is found to be between 35 and 40 atomic per cent at room temperature. Effects of alloying on lattice spacings and axial ratios are also determined. Wernick, Geller & Benson (107) used differential thermal analysis methods to obtain phase data for the six pseudobinary systems composed of combinations of $AgSbTe_2$, $AgSbSe_2$, $AgBiTe_2$, and $AgBiSe_2$ (i.e., $AgSbTe_2$-$AgSbSe_2$, etc.). For all systems complete series of solid solutions are found for the phase with cubic symmetry (i.e., $\beta$-phase). For this phase the variation in lattice parameters with composition very nearly follows Vegard's law. Studies on In-Zr (108) system for composition to about 26 weight per cent In show that In is appreciably soluble in $\alpha$- and $\beta$-phases of Zr.

Kaufmann, Cullity & Bitsianes (109) have reviewed their earlier work on the U-Si system and have pointed out the discrepancies between their earlier assignments of intermetallic compounds with the results of x-ray studies on these phases. The U-Zn system has been studied with x-ray, metallographic, and thermal methods by Chiotti, Klepfer & Gill (110). They obtained a composition diagram for the liquid-solid range at 5 atm. pressure and for a portion of the Zn(g)-U(condensed) region at 1 atm. Using cooling rate measurements Duffy & Bruch (111) were able to put boundaries on the $\delta$-phase region of the U-Zr system. A constitutional diagram for this system has been constructed by Saller, Rough & Bauer (112). Their diagram includes the intermetallic $\delta$-phase (or $\epsilon$) which is shown to be thermodynamically stable. This phase can be prepared from the elements by diffusion without going through high-temperature treatment. Results of an x-ray study of this phase ($UZr_2$) has also been reported recently (113). Wilson, Austin & Schwartz (114) studied the solubility of U in Th in relation to changes in lattice parameters and have extended the U-Th diagram on the Th rich side. The U-Bi (115) system was studied with thermal analyses and neutron diffraction by Teitel. The composition diagram of the system is presented from the author's data and results of earlier work. The intermetallic compounds $UBi_2$ and

$U_3Bi_4$ decompose peritectically. The $U_{1+x}H_3$ phase has been studied with high pressure technique by Libowitz & Gibb (116). Hills (117) has studied the phases formed in the Al-$UAl_4$, $UAl_3$-$UAl_4$, and $UAl_2$-$UAl_3$ fields in the Al-U system from etchings of samples with nitric acid, hydrofluoric acid, and chromic acid-acetic acid mixtures. The identification of the phases present in each specimen is aided by their color characteristics brought out by the etching process. A diagram for the U-Nb (118) system has been constructed from x-ray, metallographic, dilatometric, temperature-resistance measurements, and observed melting points. The diagram differs in a few details from an earlier one obtained by other investigators. Two eutectoidal points arise as a result of the two phase transitions of uranium. The Pu-Fe (119) diagram has been obtained over the complete composition range. Two intermetallic compounds $Pu_6Fe$ and $PuFe_2$ are isostructural with $U_6Fe$ and $UFe_2$, respectively. The system exhibits a low and high melting eutectic. The diagram is in essential agreement with results of previous studies of this system. Work has also been reported for the Pu-Th system (120). Plutonium is found to dissolve extensively in $\alpha$ Th and evidence is obtained for an intermetallic phase at about 32 atomic per cent Th.

*Oxide systems.*—The publication of *Phase Diagrams for Ceramists* by Levin, McMurdie & Hall (121) in 1956 makes a large amount of phase data for oxide systems readily accessible. This volume contains 811 phase diagrams from contributions of 331 scientists. Useful sections on theory, interpretation of diagrams, and experimental methods are also included. The forthcoming supplementary volume compiled by Levin and McMurdie is to contain about 500 additional diagrams. Schairer (122) has recently summarized much of the available phase data for systems of the most common ceramic oxides, $SiO_2$, $Al_2O_3$, FeO, $Fe_2O_3$, CaO, MgO, $Na_2O$, and $K_2O$. The work is an excellent review of unary, binary, ternary, and quaternary systems of these oxides. Several revised binary and ternary diagrams are included.

Phase equilibria in the Fe-Al-O system have been studied over a wide composition range by Atlas & Sumida (123). In the experiments, starting mixtures contain various amounts of Fe, FeO, $Fe_2O_3$, and $Al_2O_3$. Isothermal sections are given for temperatures of 1000°, 1250°, and 1350°C. The system involves five compounds, wüstite, iron spinel, $Fe_2O_3$, $Al_2O_3$, and $Fe_2O_3 \cdot Al_2O_3$. Complete spinel solid solution occurs between composition $Fe_3O_4$ and $FeAl_2O_4$ in the temperature range studied. Muan (124, 125, 126) has made extensive studies of the liquid-solid regions of the iron oxide-$Al_2O_3$-$SiO_2$ system in the presence of air. X-ray, quenching, and microscopic methods were used. The investigation deals with phase relationships involving the solid phases: cristobolite, tridymite, mullite, spinel, and corundum; the system has also been studied under reducing conditions where the $O_2$ pressure is controlled by the equilibrium $2\,CO_2 = 2\,CO + O_2$. A diagram illustrating the phase relationships at liquidus temperatures is presented. Newkirk & Thwaite (127) have studied the pseudoternary system CaO-$CaO \cdot Al_2O_3$-$2CaO \cdot Fe_2O_3$ in relation to its importance to portland cement chemistry. Quenching and differential thermal analysis techniques were used to study a large number of

compositions. Ternary diagrams showing final crystallization products and crystallization paths are given.

Glasser & Osborn (128) have presented phase data for the $CaO$-$Cr_2O_3$-$SiO_2$-air system from quenching runs on a large number of compositions. In the high-lime region chromium in the mixture is air oxidized. Evidence is found for a pentavalent chromium compound, $Ca_3(CrO_4)_2$. The authors have also constructed a $CaO$-$SiO_2$ diagram on the latest available data. Phillips & Muan (129) have studied the CaO-Iron Oxide system in air and at 1 atm. $O_2$ pressure. Emphasis is placed on the stability relationship involving a phase of composition $CaO \cdot 2Fe_2O_3$, the existence of which has been subject of some controversy.

Sastry & Hummel (130) studied the phase relationships in the $Li_2O \cdot B_2O_3$-$B_2O_3$ system with 20 compositions using quenching techniques. Their diagram from composition $Li_2O \cdot B_2O_3$ to pure $B_2O_3$ includes the liquid-solid region and solid-solid regions which involve the compounds $Li_2O \cdot B_2O_3$, $Li_2O \cdot 2B_2O_3$, $2LiO \cdot 5B_2O_3$, $Li_2O \cdot 3B_2O_3$, $Li_2O \cdot 4B_2O_3$, and $B_2O_3$. Hummel & co-workers (131) have also investigated the $Li_2O \cdot Al_2O_3$-$Al_2O_3$ system which consists of only one intermediate compound with composition $Li_2O \cdot 5Al_2O_3$. Electrical conductivity measurements on $PbO$-$B_2O_3$ melts have been obtained over a range of temperatures. The data indicate the formation of a two-liquid phase region in the system (132).

Jonker & Kwestroo (133) have investigated the effect of addition of small amounts of $SnO_2$ and $SrO_2$ on the $BaO$-$TiO_2$ binary. This results in the stabilization of two compounds, $2BaO \cdot 5TiO_2$ and $2BaO \cdot 9TiO_2$. The $BaTiO_3$-$SrTiO_3$ system as studied by Basmajian & DeVries (134) shows a complete series of solid solutions with no miscibility gap. A diagram for this system is proposed by the authors. The shape of the liquid immiscibility volume in the $BaO$-$B_2O_3$-$SiO_2$ system was determined by Levin & Cleek (135) from data obtained from 17 compositions. The $CaO$-$MgO$-$Al_2O_3$-$SiO_2$ system (136) has been studied in the region of the alumina apex. Information on the distribution of liquidus temperatures, primary phase fields, and quaternary invariant points was obtained and equilibrium diagrams for five triangular joins are given. Brisi (137) has reported work on the $CaO$-$SiO_2$-$CaF_2$ system. His results do not confirm the existence of a compound reported previously with composition $2CaSiO_3 \cdot CaF_2$. Reisman & co-workers (138, 139) have obtained phase data for the $Na_2O$-$Nb_2O_5$ and $KNbO_3$-$NaNbO_3$ systems from differential thermal analysis, x-ray, and density measurements. In the $Na_2O$-$Nb_2O_5$ system, two incongruent melting compounds, $Na_2O \cdot 14Nb_2O_5$ and $Na_2O \cdot 4Nb_2O_5$, and two congruent melting compounds, $Na_2O \cdot Nb_2O_5$ and $3Na_2O \cdot Nb_2O_5$, are identified. The compound $Na_2O \cdot Nb_2O_5$ is found to exist in four polymorphic forms. A phase diagram for the system over the complete composition range is constructed. The $KNbO_3$-$NaNbO_3$ system exhibits continuous solid solution in all phases.

A series of articles by Hummel & Katnack (140, 141) contain equilibrium data for $ZnO$-$P_2O_5$ (in air) and for $ZnO$-$MnO$-$P_2O_5$ systems. The former system has three congruent melting compounds $Zn_3(PO_4)_2$, $Zn_2P_2O_7$, and

$Zn(PO_3)_2$. Phase relationships for the $ZnO$-$Zn(PO_3)_2$ and $Zn_3(PO_4)_2$-$Zn(PO_3)_2$ sections are reported. Probable equilibrium relationships along the $Mn_3(PO_4)_2$-$Zn_3(PO_4)_2$ join in the $ZnO$-$MnO$-$P_2O_5$ systems are also given. Jones & Rothschild (142) used x-ray methods to obtain structural information for solid compounds formed in the $PbO_2$-$PbSO_4$ and $PbO_2$-$PbSeO_4$ systems. The oxysulphate compounds (i.e., $PbO \cdot PbSO_4$) are found to be isomorphous with the corresponding oxyselenate compounds (i.e., $PbO \cdot PbSeO_4$). The thermal decomposition of $PbCO_3$ to $CO_2$ gas and oxycarbonate compounds has been studied by Peretti (143). Two compounds of intermediate composition between $PbCO_3$ and $PbO$ are formed.

Using x-ray and dilatometric methods, Duwez (144) has investigated the $ZrO_2$-$ThO_2$ system. These results are of particular interest since they are some of the first obtained by heating specimens in a solar furnace. A tentative diagram extending to above 3000°C. is presented. Zirconia rich phases with monoclinic, tetragonal, and cubic structures are observed. The $UO_2$-$ZrO_2$ system at high temperature has been studied by Wolten (145). At 2300°C. a homogeneous phase region extending from zero to 100 per cent $ZrO_2$ is reported. Mulford & Ellinger (146) have made an x-ray study of $ThO_2$-$PuO_2$ and $GeO_2$-$PuO_2$ solid solutions. Lattice parameters for the fluorite-type structures vary linearly with mole percent $PuO_2$. The region of two immiscible liquids in the $TiO_2$-$ZrO_2$-$SiO_2$ system has recently been studied by McTaggart & Andrews (147).

The Ti-O system is one which has caused some interest in recent years because of the unusually large homogeneity range for the TiO phase. X-ray studies on the phase indicate that the NaCl-type structure has a homogeneity range between $TiO_{0.64}$ and $TiO_{1.26}$. The interesting results obtained by Andersson & co-workers (148, 149) also show that a series of phases exist with compositions between $Ti_4O_7$ and $TiO_2$. The phases identified may be represented with the formula $Ti_nO_{2n-1}$ where $n$ has values from 4 to 10. Pearson (150) has made an x-ray examination of the lower oxides of titanium. A sample with over-all composition $Ti_3O_4$ fired at 1350°C. showed only TiO and $Ti_2O_3$ lines indicating that a stable $Ti_3O_4$ phase is probably not formed in this system. Nonstoichiometric samples of TiO were also studied and a phase transition between 900–980°C. to a F.C.C. structure is reported. Andresen (151) has used neutron diffraction methods to investigate the structure of $U_3O_8$. His results indicate that structural information based on x-ray diffraction data must be in error.

Reactions of ceramic oxides with $Sm_2O_3$ and $Cd_2O_3$ have been investigated by Curtis & Johnson (152). Curtis (153) has also studied the compound formation of $Y_2O_3$ with $Al_2O_3$ and $Fe_2O_3$ at 1:1 molar ratios. Nielsen & Dearborn (154) have proposed a diagram for the $Fe_2O_3$-$YFeO_3$ system. This system is of interest because of its relation to problems of the crystal growth of magnetic garnets. Sieglaff & Eyring (155) have obtained evidence for a two phase region in Pr-O system lying between the over-all compositions $PrO_{1.83}$ and $PrO_{2.00}$ at temperatures below 350°C. and $O_2$ pressures below 10 atm.

Results of several investigations of hydrothermal reactions involving ceramic oxides have been reported recently. One aspect of this work is its bearing on geological problems. Assarsson (156, 157) studied the reactions between $Ca(OH)_2$ and $SiO_2$ at temperatures between 180° and 220°C. in an autoclave. With his technique information on reaction paths and stability ranges for compound formation may be obtained. Roy (158) has obtained information on the $CaO\text{-}SiO_2\text{-}H_2O$ system at high temperatures and pressures. Three compounds $8\,CaO \cdot 3SiO_2 \cdot 3H_2O$, $6CaO \cdot 3SiO_2 \cdot H_2O$, and $9CaO \cdot 6SiO_2 \cdot H_2O$ are reported to be stable above 700°C. at $H_2O$ pressures greater than 7500 lbs. per square inch. This work also contains results of studies on polymorphism of $Ca_2SiO_4$. Carlson (159) has studied the precipitation of compounds from calcium silicate solutions at 1°C. The work is concerned with rates of metastable phase transformations and compositions of the stable phases. Under the experimental conditions employed, the stable solid phases are believed to be gibbsite, tetracalcium aluminate hydrate, and $Ca(OH)_2$. Corwin & co-workers (160, 161) have investigated the reactions of aqueous solutions of alkaline earth oxides and silica glass under supercritical conditions. Lang & Sukava (162) have studied the $KOH\text{-}K_2CO_3\text{-}H_2O$ system at a series of temperatures between 25°C. and −60°C. The phases $KOH \cdot 2H_2O$, $KOH \cdot 4H_2O$, $K_2CO_3 \cdot 3/2H_2O$, and $K_2CO_3 \cdot 6H_2O$ are identified.

The use of differential thermal analysis methods (D.T.A.) has continued to be a valuable experimental tool for obtaining information on phase boundaries in heterogeneous systems. Newkirk (163) has described techniques and equipment for use at temperature up to 1570°C. Methods for handling volatile or nonvolatile components are discussed. Borchardt & Daniels (164) have recently applied D.T.A. methods to the study of the decomposition of inorganic hydrates. Brewer & co-workers (165, 166) have studied the $Ge\text{-}GeO_2$ and $Si\text{-}SiO_2$ systems with D.T.A. apparatus using induction heating. No evidence was found for a stable phase of composition GeO. The $Ge\text{-}GeO_2$ system is a simple eutectic type with a miscibility gap for liquids. For the $Si\text{-}SiO_2$ studies, a mixture of Si and excess $SiO_2$ was used. Under these conditions, if a stable SiO phase were formed at higher temperatures, the free silicon would be used up completely in the reaction. A peak in the D.T.A. curve occurs at a point corresponding to the melting point of silicon which indicates that the silicon was not completely reacted, and that a phase of composition SiO is not thermodynamically stable to the melting point of silicon. This system is of special interest because of the conflicting data on SiO in the literature.

Knapp & Flood (167, 168) have investigated the ionic nature of ceramic-type melts. Their procedure involves the calculation of thermodynamic activities of component A (relative to pure liquid A) in the melt in equilibrium with solid A in which component B has negligible solid solubility. In these calculations, the approximate relationship

$$-RT\ln a_A = \Delta H_f \left(1 - \frac{T}{T_o}\right)$$

is utilized, where $\Delta H_f$ and $T_o$ are the heat of fusion and the melting point of component A, respectively, and $T$ is a liquidus temperature. These values are then compared with those theoretically calculated from assumptions as to the type of model for the melt. The type of models considered are (*a*) melts consisting of undissociated molecules, (*b*) melts dissociating to simple ions, (*c*) melts dissociating to polymeric ions. Calculations for calcium metaborate indicate the presence of $(BO_2)_3^{-3}$ rings in the melt. Simple ionic models (i.e., nonpolymeric) appear applicable for many calcium borate-calcium silicate melts. Förland (169) has investigated silicate structures on $Na_2SO_4$-$Na_2SiO_3$ melts on the sulphate rich side of the phase diagram. His arguments which are based on considerations similar to that of Knapp & Flood, indicate the presence of $(SiO_3^{-2})_4$ units in the melt. Bloom & Bockris (170) have made structural interpretations for lithium silicate melts on the basis of compressibility data.

*Binary metal halide systems.*—In several articles phase data have been reported for two component systems consisting of an alkali metal halide and halides of metals in the +4 oxidation state. Barton & co-workers (171, 172) have obtained extensive data for the liquid-solid region for alkali metal fluoride-$UF_4$ and alkali metal fluoride $-ZrF_4$ systems. For these studies a combination of thermal analysis, quenching, D.T.A., and x-ray methods were used. The LiF-$UF_4$ system is found to have only incongruent melting compounds of intermediate composition. These were identified as $4LiF \cdot UF_4$, $7LiF \cdot 6UF_4$, and $LiF \cdot 4UF_4$. Five intermediate compounds were observed in the NaF-$UF_4$ system. These include $3NaF \cdot UF_4$ and $7NaF \cdot 6UF_4$ which melt congruently and $2NaF \cdot UF_4$, $5NaF \cdot 3UF_4$, and $NaF \cdot 2UF_4$ which melt incongruently. The NaF-$ZrF_4$ system shows two congruent melting compounds, $3NaF \cdot ZrF_4$ and $7NaF \cdot 6ZrF_4$ which are analogous to compounds formed in the NaF-$UF_4$ system. The compounds which melt incongruently are identified as $5NaF \cdot 2ZrF_4$, $2NaF \cdot ZrF_4$, and $3NaF \cdot 4ZrF_4$. The NaF-$ZrF_4$ system also exhibits the formation of a subsolidus compound $3NaF \cdot 2ZrF_4$ and a metastable compound $NaF \cdot ZrF_4$. The $UF_4$-$ZrF_4$ system shows a complete series of solid solution. Compositions along joins on the tinary system NaF-$ZrF_4$-$UF_4$ were also investigated. The joins $3NaF \cdot ZrF_4$-$3NaF \cdot UF_4$, and $7NaF \cdot 6ZrF_4$-$7NaF_6UF_4$ show complete solid solution series. No ternary compound was found in this system. Extensive data have also been reported for the KF-$UF_4$ and RbF-$UF_4$ systems (173). Sense & co-workers (174) have studied the NaF-$ZrF_4$ system primarily in the vapor-liquid region. Vapor pressures as a function of condensed phase composition and temperature were obtained by transpiration techniques. Their measurements also enabled them to obtain a portion of the liquidus curve on the $ZrF_4$ rich side of the diagram. Their liquidus temperatures reported are somewhat higher than those obtained by Barton & co-workers (172). Sense & Stone (175, 176) have also obtained phase data for the LiF-$ZrF_4$, RbF-$ZrF_4$, and NaF-$BeF_2$ systems in the liquid-vapor region. The NaCl-$ZrCl_4$ diagram as reported by Howell, Sommer & Kellogg (26) shows the formation of two intermediate compounds, $2NaCl \cdot ZrCl_4$ and $NaCl \cdot 2ZrCl_4$. Data for a portion of the

liquidus curve and the NaCl rich side of NaCl-HfCl diagram have been reported by Roy, Howell & Kellogg (177).

The KCl-$FeCl_2$ system has been studied by Beusman (24) and by Pinch & Hirshon (178). The two sets of data, which agree very closely, show the existence of compound $KFeCl_3$ which melts congruently and a compound $K_2FeCl_4$ which melts incongruently. Two solid-solid transitions are observed in the system. Data have also been obtained for the LiCl-$FeCl_2$ system (24). The system is quite different from KCl-$FeCl_2$ in that it exhibits behavior of complete series of solid solutions. Komarek & Herasymenko (179) investigated the NaCl-$TiCl_2$ system. A phase identified as $NaCl \cdot TiCl_2$ is found to decompose peritectically. A second phase $2NaCl \cdot TiCl_2$ decomposes in the solid state. The KCl-$ZrCl_2$ system has been studied by Duke & Fleming (180). The system has a steep liquidus curve on the KCl rich side and an intermediate compound with composition $2KCl \cdot ZrCl_2$ which melts congruently.

Seltveil & Flood (181) have used a tracer technique to define the solidus curves in binary halide systems. This method involves the addition of a small amount of a third radioactive salt to the two component system. A necessary condition is that the third component be soluble in the melt but insoluble in the solid phase. The system containing the radioactive component is heated until completely liquid and then cooled to a temperature at which solid and liquid are in equilibrium. The specific activity of the final melt is compared with that for the initial liquid to obtain the final amount of liquid phase present. Knowing the composition of the final liquid, either from analysis or from available information on the liquidus curve, together with the over-all composition and the amount of liquid phase present, it is then possible to determine the composition of the solid solution in equilibrium with melt. The method was applied to the determination of the solidus curve on the NaCl side of the NaCl-$CaCl_2$ phase diagram. Tracers of $Co^{60}$ and $Cs^{134}$ as the chloride salts were used.

*Condensed-vapor equilibria.*—The experimental studies of condensed-vapor equilibria may perhaps be divided into two general classes. These are (*a*) the determinations of phase composition; for the vapor this refers to the identification of molecular constituents and (*b*) the measurement of equilibrium vapor pressures. For calculation of thermodynamic data (i.e., heats of vaporization, etc.), it is, of course, necessary to have information from both (*a*) and (*b*). Total vapor pressure data may be obtained by static methods without prior knowledge of the vapor composition. For precise calculations of pressures with data obtained by the conventional Knudsen effusion or transpiration techniques (i.e., methods which measure weight losses), prior knowledge of the vapor composition must be available, since the pressures are functions of the molecular weights of vapor species. The torsion method, which is used in pressure range for effusion experiments, measures total pressure. A combination of torsion data and effusion data may be used to obtain information on the molecular species present in the vapor. Difficulties with the procedure arise, however, if the vapor is quite complex (i.e.,

contains a large number of polymeric species in comparable concentration.) The method is not very sensitive for the detection of minor species. Margrave (182) has suggested a modification of the effusion technique which would enable one to obtain total pressure data directly. Nesmeyanov & co-workers (183) have used an isotope exchange technique to obtain the vapor pressure of solid bismuth. The method provides high sensitivity; the pressures measured were between $10^{-8}$ and $10^{-11}$ mm. of Hg. Results of several studies of condensed-vapor equilibria utilizing a mass spectrometer for analysis of the vapor have been reported in the last few years. This method has the general advantage of high sensitivity for detection of small concentrations of minor vapor species. In general, these studies have been concerned with materials at temperatures where vapor pressures are quite low (i.e., below $10^{-2}$ mm. of Hg). The combination of effusion and mass spectrometric techniques has been used frequently. For precise pressure measurements the method requires information on ionization cross sections and detection efficiencies of ions.

A considerable amount of information on the vaporization processes for the alkali metal halides has been obtained recently. The infrared spectral studies of Rice & Klemperer (184, 185) were interpreted as indicating the pressure of only monomeric species in the vapor phase. The large amount of published data for these systems now clearly support the earlier conclusions of Friedman (186) and of Miller & Kusch (187), however, that monomeric and polymeric species are present in the vapor phase. These conclusions are based on results obtained from measurement of velocity distributions in molecular beams (20), mass spectrometric observations (21, 22, 23), torsion experiments (188), comparison of pressures determined from static measurements and apparent pressures obtained from transpiration measurements (189), and electron diffraction studies (190). Theoretical considerations (191, 192) for the dimer molecule [i.e., $Na_2F_2(g)$] also indicate the species to be quite stable. The available data for these systems lead to the following general considerations. In all cases studied mass spectrometrically, detectable concentrations of dimer molecules were found. For each halide series the dimer stability (i.e., absolute magnitude of the dimerization energy) increases in the sequence cesium halide to lithium halide. For a series of halides of the same alkali metal the stability of the dimer increases in the sequence from iodide to fluoride. For the alkali fluorides which are the lowest in relative volatilities, the ratio of dimer to monomer will increase in the solid-vapor region with increasing temperature. In the liquid-vapor region the ratio of dimer to monomer will not increase rapidly with increasing temperature which implies that the heats of vaporization of monomer and dimer of the same alkali-metal fluoride are nearly equal. The lithium halide vapors contain appreciable concentrations of trimer molecules. In the LiF system the trimer concentration is relatively large. On the basis of the available data the trimer of LiF should become an important chemical species near the boiling point.

The vapor pressure studies of Sense & co-workers for two component fluoride systems are interpreted as evidence for the existence of complex fluoride molecules in the vapor phase. Work on the $NaF$-$BeF_2$ system (176) indicates the probable existence of a $NaBeF_3$ complex. In their calculation of the partial pressures of alkali fluoride molecules from transpiration measurements the molecular weight for the monomer was used. It is certainly true, however, that appreciable concentrations of dimer molecules will also be present in the vapor phase in the alkali halide-rich region under their experimental conditions.

Results of several mass spectrometric studies on the vaporization processes in oxide and carbide systems have also been reported. The vapor phase for systems such as $MoO_3$ and $V_2O_5$ are found to be quite complicated in that they contain a large number of polymeric species. Results of these investigations account for many of the earlier difficulties encountered in interpreting vapor pressure data for many of these systems. Several metal carbide systems have been studied mass spectrometrically. The vapor phase of SiC (193) is particularly interesting. The molecular species which have been identified include SiC, $SiC_2$, $Si_2C$, $Si_2C_3$, and $Si_3C$.

TABLE I

MOLECULAR SPECIES IN SOME CONDENSED-VAPOR SYSTEMS

| Condensed System | Temp. Range[a] °K. | Major Vapor[b] Species | Minor Vapor[b] Species | Reference |
|---|---|---|---|---|
| *Metallic systems* | | | | |
| B | 2100–2400 | B | $B_2$ | 197 |
| Bi | 479–532 | Bi | $Bi_2$ | 183 |
| Fe | 1500 | Fe | | 30 |
| Cr | 1370–1500 | Cr | | 30 |
| La | 1640–2017 | La | | 198 |
| Ce | 1611–2038 | Ce | | 198 |
| Eu | 700–900 | Eu | | 199 |
| Pd | 1388–1675 | Pd | | 200 |
| Tm | 809–1219 | Tm | | 201 |
| Te | 750–1130 | $Te_2$ | | 202 |
| Se | 550–900 | $Se_2$ | $Se_3$ | 203 |
| Ag, Au, Cu | 1300–1750 | Ag, Au, Cu | $Ag_2$, $Au_2$, $Cu_2$ | 17, 18 |
| *Oxides* | | | | |
| $Li_2O$ | 1250–1550 | Li, $O_2$, $Li_2O$ | LiO | 204 |
| BeO | 1873–2273 | Be, O, $O_2$, $(BeO)_2$ $(BeO)_4$ | Other polymetric species | 205 |
| $MoO_3$ | 800–1000 | $(MoO_3)_3$ | $(MoO_3)_4$, $(MoO_3)_5$ | 206 |
| $WO_3$ | 1330–1450 | $(WO_3)_3$ | $(WO_3)_4$, $(WO_3)_5$ | 207, 208 |
| Ta—$Ta_2O_5$ | 2000–2300 | TaO, $TaO_2$ | | 209 |
| Zr—$ZrO_2$ | 2100–2500 | ZrO | | 210 |
| Ta—$ZrO_2$ | 2400–2500 | TaO,ZrO | | 210 |
| Ti—$Ti_2O_3$ | 1700–2100 | TiO, Ti | $TiO_2$ | 211 |
| V—O | 1680–1950 | VO, Polymeric Species | Polymeric species | 212 |
| $B_2O_3$ | 1400–1625 | $B_2O_3$ | | 213 |
| B—$B_2O_3$ | 1294–1457 | $B_2O_3$ | $B_2O_3$ | 214 |
| B—MgO | 1337–1375 | $B_2O_3$ | | 197 |

TABLE I—(*continued*)

| Condensed System | Temp. Range[a] °K. | Major Vapor[b] Species | Minor Vapor[b] Species | References |
|---|---|---|---|---|
| $GeO_2$ | 1313–1373 | GeO, $O_2$ | | 215 |
| Ta, W—oxides | | | | 216 |
| *Carbides* | | | | |
| $Mn_7C_3$ | 1073–1223 | Mn | | 217 |
| Fe—C (austenite) | 1400–1670 | Fe | | 218 |
| Al—C | 2100 | Al | $Al_2C_2$ | 219 |
| Be—C | 1430–1669 | Be | | 219, 220 |
| Ga—C | 1600 | Ga | $Ga_2$, $Ga_2C_2$ | 219 |
| Ti—C | 2500 | Ti | $C_3$, $C_2$, C | 219 |
| Si—C | 1700–2300 | Si, $SiC_2$, $Si_2C$ | $Si_xC_y$ | 191 |
| $BaC_2$—C | 1355–1671 | Ba | | 221 |
| $BC_x$—C | 2200–2500 | B | | 222 |
| *Halides* | | | | |
| LiF | 1000–1330 | Monomers & dimers | Trimers and | 20, 22, 23, 173, 188 |
| NaF | 1000–1250 | in various relative | tetramers | 20, 22, 23, 174, 188 |
| KF | 900–1100 | abundances | | 20, 23, 188 |
| RbF | 950–1330 | | | 20, 175, 188 |
| CsF | 750–900 | | | 20, 188 |
| Alkali, Chlorides, Bromides, Iodides | | Monomers & dimers | Trimers | 19, 21, 22 |
| LiF—NaF | 1000 | Monomers, dimers $NaLiF_2$ | Trimers | 23 |
| LiF—$ZrF_4$ | 943–1333 | Monomers & dimers | Complex molecules | 175 |
| NaF—$ZrF_4$ | 1100–1350 | of alkali fluoride, | | 174 |
| RbF—$ZrF_4$ | 963–1333 | $ZrF_4$ | | 175 |
| NaF—$BeF_2$ | 770–1330 | NaF, $Na_2F_2$, $BeF_2$ | $NaF \cdot BeF_2$ | 176 |
| $BeF_2$ | 1070–1300 | $BeF_2$ | | 176 |
| $ZrF_4$ | 980–1100 | $ZrF_4$ | | 27 |
| $ZrCl_4$ | 480–740 | $ZrCl_4$ | | 223 |
| $HfCl_4$ | 476–681 | $HfCl_4$ | | 223 |
| $ThF_4$ | 1055–1600 | $ThF_4$ | | 224 |
| Gallium and Indium Halides | | | | 225 |
| Ag, Cd, Zn, Pb—Halides | | | | 226 |
| KCl—$FeCl_2$ | 1000–1340 | KCl, $FeCl_2$ | $Fe_2Cl_4$, $KFeCl_3$ | 24 |
| LiCl—$FeCl_2$ | 1000–1330 | LiCl, $FeCl_2$, $Li_2Cl_2$ | Polymers, complexes | 24 |
| $FeCl_2$ | 980–1167 | $FeCl_2$ | $Fe_2Cl_4$ | 24 |
| $FeCl_3$ | 597–685 | $FeCl_3$ | $Fe_2Cl_4$ | 227 |
| *Hydroxides* | | | | |
| $Mg(OH)_2$ | 413–503 | $H_2O$ | | 195 |
| $ZnO-H_2O$ | 1573 | $Zn(OH)_2$ | | 228 |
| NaOH | 573–723 | $Na_2(OH)_2$, probably $H_2O$ | NaOH | 229 |
| NaOH | 573 | $H_2O$ | | 194 |
| KOH | 573–723 | $K_2(OH)_2$, KOH | | 230 |
| NaOH—KOH | 600–700 | Monomers, dimers $NaK(OH)_2$ | | 231 |
| *Miscellaneous* | | | | |
| $Cu(NO_3)_2$ | 430–496 | $Cu(NO_3)_2$ | | 232 |
| InP | 973–1318 | $P_4$ | | 233 |
| $TaSi_x$ | 2100–2500 | Si | | 234 |

[a] Where several references are given, the combined temperature range is indicated.
[b] For some systems species are inferred by the reviewer, not necessarily by the references indicated.

The alkali hydroxides have also been found to vaporize largely as dimer molecules, showing behavior analogous to the halides. Kay & Gregory (194) have obtained evidence from effusion experiments that the decomposition pressure of $H_2O$ from NaOH is higher than that predicted on the basis of available thermodynamic data. They have also studied the decomposition of $Mg(OH)_2$ (195) to MgO and water vapor by the same method. The decomposition pressures of $H_2O$ were found to be time dependent, falling below the expected saturation values and were also found to depend on the orifice size, indicating that the accommodation coefficient of water is small.

Some condensed-vapor systems for which data have been reported in 1957–1958 are presented in Table I. A comprehensive tabulation of vapor pressure data for metals is found in Stull & Sinkes's *Thermodynamic Properties of the Elements* (196).

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# SOLUTIONS OF ELECTROLYTES[1]

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Due to limitations of both space and time, the reviewer has restricted the scope of the following review, omitting certain subjects which might properly be included. Notable among these are: solutions of electrolytes in molten metals and salts, solutions of polyelectrolytes and soaps, solutions of chelate complexes, phase studies with water as one component, ion exchange, electrode processes, and nuclear magnetic resonance. These topics are left to reviews, under other titles, appearing at least occasionally in the *Annual Review of Physical Chemistry*.

The reviewer does not disguise his enthusiasm for theoretical work, especially that with a statistical mechanical flavor.

The most recent discussion of The Faraday Society, *Interaction in Ionic Solutions* (1), has been published. In this one volume a number of very significant and stimulating articles are contained or discussed. Most of the papers are mentioned individually below.

## Equilibrium Properties

*Theory.*—During the past year, considerable progress has been made in this field. Falkenhagen & Kelbg (2) have briefly reviewed recent work in the statistical theory of ionic solutions and have presented a derivation of the relation between the potential of average force and the mean electrostatic potential employed in the Debye-Hückel theory.

A new theory which, for I-I electrolytes, has been carried through to a comparison with osmotic coefficient data is due to Möller (3). The starting point is the Born-Green integral equation in the multicomponent form previously presented by Kelbg & Möller (4). The Kirkwood superposition approximation is contained in the initial integral equations; other limitations are introduced while solving the equations, a process which contains some novel features. The initial equations are integral equations for the potential of average force, $\Phi_{\sigma\tau}(r) - kTf_{\sigma\tau}(r)$, on a particle of type $\tau$ at a distance $r$ from a central particle of type $\sigma$. The first term $\Phi_{\sigma\tau}(r)$ is the direct intermolecular potential; the model is the usual one of charged hard sphere ions in a structureless solvent of macroscopic dielectric constant $D$. The unknown functions $f_{\sigma\tau}(r)$ also appear in the integrand as $\exp f_{\sigma\tau}$. In this theory these exponentials are linearized, then assumed to be slowly varying functions of distance, and, as a first approximation, replaced by a mean value $\epsilon$ independent of the species $\sigma$ and $\tau$. The equations are then solved for $f_{\sigma\tau}(r)$ by using Fourier transforms along with the following approximations: all distances of closest approach are the same, $a$; $\exp \Phi_{\sigma\tau}(r)$ may be linearized in the inte-

[1] The survey of the literature was completed in December, 1958. The Russian literature is partly reviewed.

grand, and therefore the final equations may be expected to be invalid when $a$ is very small and $\Phi_{\sigma\tau}$ consequently large in part of the range of integration. Two further approximations are made which (it is claimed) affect only terms in concentration of order higher than first. There results a formula for $f_{\sigma\tau}(r)$ still containing the unknown mean value $\epsilon$, the first approximation to the slowly varying function of $r$. This function is determined by requiring that the charge density far away from the central ion vary with $r$ as does the Debye-Hückel form, $e^{-\kappa r}/r$, where $\kappa$ is the Debye-Hückel kappa, and electrical neutrality determines the constants, thus $\epsilon^2 = 1 + be^{-\kappa r}$ where $b$ is a moderately complicated function of $\kappa a$. Self-consistency requires $\epsilon$ to vary only slowly with $r$ and therefore $be^{-\kappa a}$ must not be too large. Calculations lead the author to estimate that $\kappa a$ should not be larger than about 0.5. Knowing $f_{\sigma\tau}(r)$, one then obtains the potentials of average force, the radial distribution functions, the osmotic pressure, and finally the osmotic coefficient. Comparison with the earlier calculations of Haga (5), based on Mayer's (6) theory of ionic solutions and presumably correct to a higher power of concentration than Möller's expression, indicates the limitations of Möller's theory (invalid at moderate concentration, small $a$, and large $\kappa a$). Judging by agreement with experimental data, the two theories appear comparable though the lack of data at low concentrations makes a comparison very difficult. It is obvious that the theoretical problem is by no means completely solved.

For multicomponent systems, expansions in powers of the particle densities have been derived by Meeron (7) for (*a*) the potential of average force among any number of particles and (*b*) the distribution function among those particles. Subsequently, Meeron (8) has applied this difficult theory to the case of two ions in an ionic solution. Formal approximations correct through terms linear in the concentration are presented and compared with earlier work of Mayer (6) and Kirkwood & Poirier (9).

A paper by Tolmachev & Tiablikov (10) is concerned with the statistical mechanical basis of Bjerrum's theory of ionic association. For the Debye model, a first order solution of Bogoliubov's (11) integral equation for the pair correlation function of two ions is found. The free energy due to interionic interaction which is obtained approximately from this pair correlation function becomes, for small degrees of association, identical with the Bjerrum expression.

Guggenheim (12) has emphasized the distinction between the Debye-Hückel model and the Debye-Hückel approximation, the linearization of $\exp(Ze\psi/kT)$. A comparison of the potential at the surface of an ion due to the ionic atmosphere, as given by the Debye-Hückel approximation, with the value obtained by the numerical integration method of Müller (13), leads to the conclusion that for II-II salts the Debye-Hückel approximation is good only for distances of closest approach larger than about 10 A. Using a distance slightly greater than this as both the distance of closest approach of the free ions and the "association distance" in a formula for the osmotic

coefficient, only slightly different from Bjerrum's (14) (but derived in a novel and admittedly nonrigorous fashion), good agreement is obtained with the data on very dilute solutions of $CuSO_4$, $ZnSO_4$, $MgSO_4$, $CaSO_4$, $CoSO_4$, and $NiSO_4$ obtained by Brown & Prue (15). The calculated osmotic coefficients are very insensitive to the exact value of the "association distance" in the range 10–14 A, whereas the association constant varies by 20 per cent. The conclusions are that for these salts the Debye-Hückel model is good, but the simple Debye-Hückel approximation is not good at concentrations larger than $10^{-5}$ $M$. The widely used Davies equation for the activity coefficient is discussed.

Fuoss (16) has reconsidered the equilibrium between ion pairs and free ions, now requiring physical contact as the criterion for an ion pair. The model used for the derivation of the association constant consists of a dielectric continuum containing cations of finite size penetrable to point-charge anions, the interior of a cationic sphere being a region of constant electrostatic potential. The model thus provides a region of space within which the model anion forms an ion pair, artificially providing for what is referred to as the ion-trapping tendency of a real ion in a real (discontinuous) solvent. The association constant $K_a$ is found by requiring that an added differential number of anions distribute themselves between ion pairs and free ions in the ratio of the total cationic volume to the solution volume, weighted by an electrostatic Boltzmann factor. In this step the potential everywhere outside a cation is taken as zero. The Debye-Hückel approximation is found for the activity coefficient of a free ion. Whatever may be said concerning the rigor and self-consistency of this treatment, there results $K_a = 2.524 \times 10^{-3} \mathring{a}^3 e^b$ (where $\mathring{a}$ is the cation radius in angstroms and $b = \epsilon^2/aDkT$) which does vary with $D$ in the manner found by Denison & Ramsey (17) and Gilkerson (18). The new $K_a$ is larger by a factor $b$ than the asymptotic form (for large $b$) of Fuoss & Kraus' (19) earlier expression for $K_a$. A re-evaluation of data thus seems to be appropriate.

The intermolecular potential between two dissolved ions is expressed as a coulombic term plus a short range potential. The latter, for reasons of simplicity and the lack of anything better, has commonly been taken as a hard sphere cutoff potential or, less commonly, has been considered as a variation of the dielectric constant with interionic distance. A notable contribution to the theory of the short range potential is the paper of Levine & Wrigley (20). The model consists of two ions, around each of which four dipolar water molecules are tetrahedrally co-ordinated with dipoles pointing either toward or away from the center of the ion, depending on its electrical sign. Outside these spherical hydrated ions, the solvent is a continuous medium of uniform macroscopic dielectric constant $D$. At two arbitrary points, one inside a hydrated ion and one outside, the electrostatic potential is approximated by the first three terms of an expansion in spherical harmonics. Seven constants appearing in these expansions must be determined, for the charge distribution within each hydrated ion is not known when the ions

are separated by a finite distance. Two of these constants, the dipole and quadrupole moments of the hydrated ion, are found in terms of the polarizabilities of the ion and of the water molecule, the dipole moment of water, etc., by considering the reaction field caused by the other hydrated ion and the dielectric. Electrostatic boundary conditions at the surface of the hydrated ion provide the other relations needed, the equations are then solved by successive approximations. With the constants known, so is the potential at every point and hence the field intensity. The potential energy $V(R)$ as a function of interionic separation $R$ is found by adding ($a$) the work necessary to polarize the two isolated hydrated ions *in vacuo* to the condition which will be the equilibrium one at $R$ with the dielectric present, ($b$) the work of bringing the two polarized hydrated ions *in vacuo* from infinity to $R$, and ($c$) the work of introducing the dielectric. The work of introducing the dielectric when the unpolarized ions are at infinite separation is then subtracted, yielding the final expression

$$V(R) = \frac{\epsilon^2}{DR}\left[\pm 1 + b_3\left(\frac{a}{R}\right)^3 + b_5\left(\frac{a}{R}\right)^5 + b_6\left(\frac{a}{R}\right)^6 + \cdots\right] \qquad 1.$$

The $b$'s are known complicated functions of $D$, ionic polarizability, etc., and vary slowly with $a/R$ but in such a way that the smallest (negative) power of $R$ is correctly given by the exponent shown in 1. The magnitude of the short range terms is appraised in a calculation appropriate to KF. An uncertainty in the radius $a$ of the hydrated ion, which might range from 4.09 A (sum of ionic radius and water diameter) to 3.09 A (distance of closest penetration of solvent) fortunately has little effect on the calculated $V(R)$. At $a/R = \frac{1}{4}$, the sum of the three correction terms is 0.8 per cent of the coulombic term, while at $a/R = \frac{1}{2}$ (contact) the sum is about eight per cent of the coulombic term. In this case the short range potential is always positive (repulsion) regardless of the signs of the two ions, although with larger polarizabilities a negative (attractive) correction might occur. Although very complicated, this calculation appears sound, is capable of extension and refinement, and should serve to congeal our ideas of short range interionic potentials.

An extension of the Debye theory of the salt effect to higher concentrations has been reported by Baranowski & Sarnowski (21).

*Solvation.*—This reviewer is intrigued by the multiplicity of current views on solvation. A good review of the present position of one large school of thought has been given by Frank & Wen (22). The idea of "icelikeness" in small regions of aqueous solutions is made more precise by the notion of a "flickering cluster" of hydrogen-bonded water molecules.

An exposition of a different approach which has been used for some time in the Russian literature has been presented in English by Samoilov (23). Rejecting the chemical concept of one or more hydration shells except as a limiting case, this theory deals with the mean length of time between exchanges of adjacent water molecules. Positive hydration is the lessening of

this time for a water molecule at the surface of an ion. The time ratios are related (exponentially) to an activation energy for the exchange, which in turn is related to the temperature dependence of the ionic mobility and of the coefficient of self-diffusion of water by an equation derived by Samoilov (24). The activation energy is found to be negative for $K^+$, $Cl^-$, and larger univalent ions; compared with bulk water, water molecules at the surface of these ions have a shorter exchange time and the ions are "negatively" hydrated. Experimental evidence corroborating this conclusion is adduced.

A critique of methods of finding solvation numbers has been presented by Haase (25). Requiring them to be purely phenomenological quantities, independent of both structure and (by inference) the microscopic mobility of water, he presents a method whereby solvation numbers could be determined if Hittorf transference numbers and the number of moles of solvent carried from anode to cathode by one Faraday were known. In the absence of an accurate knowledge of the latter quantity, a self-consistent method starting with hydration numbers for $Li^+$ and $Na^+$ calculated by the method of Robinson & Stokes (26) is presented.

Brady & Krause (27) and Brady (28) have calculated radial distribution functions (in electron units) from x-ray diffraction data on concentrated aqueous KOH, KCl, and LiCl. The interpretation consists of finding a set of hydration numbers which with crystallographic ionic radii and some assumed solution structure semiquantitatively reproduces the location of and area under the peaks in the experimental curves. Except for $Cl^-$, calculated ionic energies of hydration agree well with Latimer, Pitzer & Slansky's (29) values. From their own x-ray diffraction data on water from 0°C. to 60°C. and 1.44 *M* aqueous HCl, KOH, KCl, and $CaCl_2$, van Panthaleon van Eck, Mendel & Boog (30) reach generally different conclusions. A critical comparison with the work of Brady & Krause is difficult because the Dutch group treat the raw data differently and base their interpretation on octahedral, not tetrahedral, co-ordination in pure water as deduced from the location of the first peak (31).

Miller (32) has used the symmetry of the electric field about solvated $Eu^{+3}$ derived from spectroscopic measurements on solutions of $EuCl_3$ in water and methanol to eliminate a number of conceivable structures for the solvate. Miller proposes that $Eu^{+3}$ in water occupies a certain interstitial position of the ice III structure. Considering only the eight nearest neighbors, this lattice fragment has the correct symmetry and a nearly large enough hole. In methanol, the proposed solvate structure of lower symmetry contains two fragments of the solid methanol lattice. Ion pair formation would not be expected to disturb the spectroscopic symmetry. The same general approach is apparent in a paper by Krumholz (33) on the spectrum of aqueous $Nd^{+3}$, although no detailed solvate structures are proposed.

Proceeding in part from a separation of his (34) partial molal heat capacity data into ionic contributions, Ackermann (35) has concluded that in water the proton is "primarily" bound to four water molecules and "sec-

ondarily" to four at 0°C., one at 130°C. For $OH^-$, the author proposes six "primarily" bound and seven (at 0°C.) to three (at 130°C.) "secondarily" bound water molecules. Dielectric and spectral data are cited in support.

The orientational energy of a water molecule in the field of a cation and its variation with ionic radius has been considered by Osipov & Shelomov (36).

Reynolds (37) has obtained values for the standard free energy of reorientation of water molecules from that orientation about ferrous ion to that about ferric ion. Calculations based on two relatively simple electrostatic models give 26 and 41 kcal./mole, bracketing 31 kcal./mole obtained by a thermochemical cycle. This latter method gives 41 and 44 kcal./mole for $Cr^{+2}$ and $V^{+2}$, respectively. The author concludes that these values, although considerably higher than 8.1 kcal./mole assumed by Marcus, Zwolinski & Eyring (38), are low enough for electron tunneling to be a feasible mechanism for oxidation.

Strehlow & Koepp (39) have electrolyzed 1.0 *M* and 0.1 *M* $AgNO_3$ solutions in a mixed solvent, water with 0.55 mole per cent to 94.2 mole per cent acetonitrile. The ensuing difference in the composition of the electrode compartments gives information about the preferential solvation of $Ag^+$ with acetonitrile rather than with water (and vice versa for $NO_3^-$). Although solvation numbers are not uniquely determined by the data alone, additional reasonable approximations yield the four solvation numbers as a function of solvent composition. The application of Walden's rule is discussed.

Horne (40) has suggested that rate data on reactions between ferrous and ferric complexes is consistent with the existence of a ferric monoperchlorate complex. However, Horne (41) has concluded that the intensification of the yellow color of ferric perchlorate solution by alcohols is not a result of the formation of a ferric perchlorate complex, but of the replacement of water in the solvation sphere of a ferric hydrolysis product by alcohol molecules.

Pullin & Pollock (42) have examined the infrared spectra of acetone solutions of $AgClO_4$ and $LiClO_4$; they suggest that disolvates are present. Fogg (43) has measured the velocity of ultrasound in acetone solutions of $LiClO_4$ and $Ca(NO_3)_2$. The derived solvation number of the former salt is 1.35 (increasing steadily with increasing dilution toward 4) at the concentration at which Pullin & Pollock propose 2. A concentration independent solvation number of 2 is obtained for $Ca(NO_3)_2$.

Using microwaves, an extensive study of the dielectric behavior of aqueous solutions of six salts and two acids (over a range of frequency, concentration, and temperature) has been reported by Hasted & Roderick (44). They derive the number of hydrogen bonds effectively broken per ion and, separately, the number of water molecules prevented by an ion from rotating in an electric field. The relation of these to the "hydration" number depends on structural details, making quantitative interpretation very difficult. Data on methanolic and ethanolic solutions of five salts at 20°C. present even greater interpretive difficulties.

Solvent structure in strong acid solutions has been discussed by Wyatt (45), Bascombe & Bell (46), and by Gupta, Hills & Ives (47). Diamond (48) has qualitatively explained the order of activity coefficients found for strong I-I and II-I electrolytes in terms of water-structure breaking and tightening, and localized hydrolysis.

*Complexes and ion pairs.*—In this section, articles dealing with ion pairs are intermixed with those dealing with complexes. This is done, not with the malicious intent of agitating already turbid waters, but because there appears to be no universally accepted differentiation, especially on the operational level. An ion pair will be so labelled when the author cited so labels it.

A new method for determining the formulas of complexes by utilizing ion exchange has been described by Cady & Connick (49), who therewith establish the existence of aqueous $Ru^{+3}$, $RuCl^{+2}$, and (presumably) $RuCl_2^{+}$. A general method for the determination of dissociation constants of optically active weak acids has been presented by Nebbia (50). Application to ascorbic acid, glutamic acid, and lysine gives good agreement with published values. A potentiometric technique for determining dissociation constants of unstable weak acids previously developed by Caramazza (51) and applied to HOCl has now been applied to cyanic acid (52). The p$K$ value found drops from 3.76 at 0°C. to 3.37 at 35°C., then increases to 3.48 at 45°C. Thermodynamic functions for the dissociation are calculated. New spectrophotometric methods have been devised by Ang (53) for "overlapping" ionization constants, by Sakellaridis (54), and by Colleter & Romain (55) for the simultaneous determination of formulas and dissociation constants. Monnier & Kapétanidis (56) have devised a method for determining dissociation constants of weak acids from pH titration curves. The method, usable for "overlapping" dissociation constants, is based on Bjerrum's (57) formation function for the case where the ligand is a proton. Excellent agreement with published dissociation constants for oxalylhydroxamic acid is obtained; for ethylene glycol *bis*-(β-aminoethylether)-N,N′-tetraacetic acid the authors report $1.45\times10^{-2}$, $6.18\times10^{-4}$, $3.90\times10^{-10}$, and $2.73\times10^{-11}$ for the four dissociation constants. A number of restrictions on the use of Job's method have been discussed by Jones & Innes (58).

The following work on the dissociation of acids has appeared. The three apparent dissociation constants of phosphoric acid at 38°C. at ionic strengths $\mu$ of 0.1 $M$ to 0.5 $M$ can be represented as $pK_i = A_i - B_i\mu^{1/2}$, with $A_1 = 2.120$, $B_1 = 0.467$, $A_2 = 6.944$, $B_2 = 0.562$, $A_3 = 12.185$, $B_3 = 1.494$, according to Elliot, Sharp & Lewis (59). For isocitric acid at 25°C., Hitchcock (60) reports p$K$ values of 3.287, 4.714, and 6.396. Schwarz & Müller (61) report $K_1 = 1.24\times10^{-10}$ for monosilicic acid. From a careful potentiometric and spectrophotometric study in which the Davies equation was employed for the activity coefficients, Howard, Nair & Nancollas (62) derive $3.0\times10^{-7}$ for the dissociation constant of $HCrO^{4-}$ at 25°C. Čůta, Beránek & Písecký (63) report $7.1\times10^{-8}$ for the dissociation constant of $HSO_3^{-}$. From a variety of measurements and a few estimates, Wood (64) arrives at a value of p$K$ of

15.0 ± 0.6 for the dissociation of $HSe^-$ at 22°C. Davidenko (65) has determined the dissociation constants of trihydroxyglutaric acid potentiometrically, finding $K_1 = 8.4 \times 10^{-4}$, $K_2 = 6.1 \times 10^{-5}$ at 20°C. A precise emf. method employing the Davies equation has been used by Nair & Nancollas (66) to determine the dissociation constant of $HSO_4^-$ from 0°C. to 45°C. The derived heat, entropy, and free energy of dissociation agree well with Pitzer's (67) calorimetric values. Mattoo (68) reports p$K$ values for the dissociation of three monohydroxy substituted 4-methyl coumarins at 25°C.; for the 5-hydroxy, 8.26; for the 6-hydroxy, 9.14; and for the 7-hydroxy, 7.80. Riccardi & Bresesti (69) report spectrophotometrically determined p$K$ values for the dissociation of the conjugate acids of quinoline and all its monomethyl derivatives in aqueous solution at 20°C. The values found are p$K = 4.96$, p$K_2 = 5.83$, p$K_3 = 5.17$, p$K_4 = 5.67$, p$K_5 = 5.20$, p$K_6 = 5.22$, p$K_7 = 5.34$, and p$K_8 = 5.05$; the subscript indicates the position of the methyl group. Zimmerman (70) presents the dissociation constant for glucosammonium ion determined potentiometrically from 15°C. to 50°C. in the form $\log K_a = 73.00 - (16089/T) + 9.16 \log T - 0.1704T + 0.00001600T^2$. Saito, Manabe & Yui (71) present $\log K = (214.58/T) + 3.71481 \log T - 16.7984$ for the dissociation constant of tropolone from 10°C. to 40°C. as determined from emf. measurements. For hinokitiol in the same temperature range, $\log K = (1974.9/T) + 20.2880 \log T - 63.9840$.

The following work on hydrolysis may be noted. Achenza (72) reports first hydrolysis constants for aqueous $Zn^{+2}$ and $Cu^{+2}$; at 25°C. he finds p$K_1$ values of 9.36 and 7.34, respectively. By an analysis of potentiometric titration curves Lefebvre (73) concludes that in the hydrolysis of aqueous $Th^{+4}$ ion the important species present are $Th(OH)_2^{+2}$, $Th_2(OH)_2^{+6}$, and $Th_5(OH)_{12}^{+8}$. The first hydrolysis constants for aqueous $Nd^{+3}$ and $Pr^{+3}$ have been determined by Tobias & Garrett (74), who report p$K_a = 8.5 \pm 0.4$ for both ions at 25°C. Their study is concerned primarily with the solubility of $Nd(OH)_3$ and derived thermodynamic functions. The hydrolysis of $Sn^{+2}$ at 25°C. and an ionic strength of 3 $M$ has also been investigated by Tobias (75), who reports the following p$K$ values for the formation of $Sn_i(OH)_j^{2i-j}$ from $i$ $Sn^{+2}$ and $j$ $H_2O$: $6.77 \pm 0.03$ for $i = 3, j = 4$; $4.45 \pm 0.15$ for $i = 2, j = 2$; and $3.92 \pm 0.15$ for $i = 1, j = 1$.

Smithson & Williams (76) have suggested that ion pairs might be differentiated from complexes whenever transition metal ions are involved by examining two bands in the spectrum of the solution. Since the levels of the charge transfer band (in the ultraviolet) presumably vary as a small negative power of the ion-ligand separation, probably as $r^{-1}$, this band should be affected by both complex formation (ligand adjacent to metal ion) and ion-pair formation (one or more solvent molecules between ligand and metal ion). The band in the visible region results from forbidden transitions among $d$ states split by polarization of the ion by the ligand. Since this polarization varies as a large negative power of $r$, perhaps $r^{-5}$, this band should be affected by complex formation but not by the spatially more remote ion-pair forma-

tion. Some published data is presented in support of this view. The authors' own spectroscopic data on solutions of $Co^{+2}$ indicates complex formation with $CNS^-$, $Cl^-$, and $S_2O_3^{-2}$, and (circumstantially) ion-pair formation with $NO_3^-$ and $SO_4^{-2}$. At sufficiently high $SO_4^{-2}$ concentrations, a complex is apparently formed. Cohen's (77) relevant critique points out that the definition of an ion pair in the Bjerrum-Fuoss sense involves a statistically defined distance (essentially the minimum in the ion-partner radial distribution curve), which in general will differ from the distance at which spectral changes vanish. The spectroscopically determined concentration of ion pairs will lead to association constants differing considerably from the statistically defined association constant. Smithson & Williams do not determine the association constant for $Co^{+2}$ with $SO_4^{-2}$, but suggest that activity coefficients might be used to do this once it is shown that ion pairing rather than complexing occurs.

Heats and entropies of formation of a large number of ion pairs have been collected or measured by Nancollas (78). His qualitative interpretation follows in part Gurney's (79, 80) separation of the work of formation into that resulting from a long range electrostatic force and that resulting from a short range force. The hydroxide ion pairs are shown to fall into two groups; those with only moderately large association constants and positive $\Delta H$ of association are those of cations (e.g., $Ca^{+2}$) with rare gas structure, small repulsive short range forces, and an association constant therefore controlled by the temperature variation of the dielectric constant. The other group, with very large association constants and negative $\Delta H$ of association are those of cations (e.g., $Fe^{+3}$) not having a rare gas structure, but having large quantum mechanical attractive forces progressively opposed by increasing thermal agitation. Also presented are correlation studies involving the entropy of hydration of the ion pair.

From conductance measurements at 25°C., 35°C., and 45°C., Flaherty & Stern (81) have calculated dissociation constants for the tetrabutylammonium picrate ion pair in *o*-dichlorobenzene by Shedlovsky's (82) method and in chlorobenzene and *m*-dichlorobenzene by Fuoss & Kraus' (83) method. In the course of a critical comparison of Bjerrum's (14), Denison & Ramsey's (17) and Gilkerson's (18) theories, it is shown that for these systems the values of $\Delta H°$ and $\Delta S°$ predicted by the first two theories are much less than the experimental ones, while no values can be predicted using the last named theory. Panckhurst & Woolmington (84) have made an unusually careful spectrophotometric study of the association of $Fe(CN)_6^{-4}$ with $Tl^+$ and $La^{+3}$. Activity coefficients are calculated from the Davies equation and calculated dissociation constants $K$ are considered significant only when effectively independent of the value assumed for the empirical coefficient of the term linear in $c$. For $TlSO_4^-$, $K$ is of order 0.1, too large for this to be true. At 25°C., 35°C., and 50°C., $10^4\,K$ for $TlFe(CN)_6^{-3}$ is 10.1, 8.9, and 8.7, respectively, requiring a Bjerrum distance of 2.7 A. For $LaFe(CN)_6^-$, $K = 8.7 \times 10^{-6}$, corresponding to a more reasonable 6.6 A. A

discussion of the spectrophotometric method for ion pairs is presented by Bale *et al.* (85). The hazards of high ionic strengths are exposed [see Davies & Monk (86)]. Taking $CuSO_4$ as an example, Davies, Otter & Prue (87) illustrate the extent to which the dissociation constant of an ion pair depends on the association distance assumed in the calculations.

The following association constants have been reported: 0.76 for $NaP_3O_9^{-2}$ and $1.4\times10^{-3}$ for $Na_2P_3O_9^-$ by Indelli (88) potentiometrically; 1090 for $FeCNS^{+2}$ and 40 for $Fe(CNS)_2^+$ at 18°C. by Perrin (89) spectrophotometrically; 5.0, 5.4, 5.4 for $ZnF^+$ and 5.2, 5.0, 5.6 for $CuF^+$ (all ±20 per cent) at 15°C., 25°C., and 35°C., respectively, by Connick & Paul (90); for the ion pairs $MgSO_4$ and $ZnSO_4$ from 0°C. to 45°C. by Nair & Nancollas (91) from emf. measurements using the Davies equation. After an extensive investigation, Banerjee, Sen Gupta & Siddhanta (92) and Siddhanta & Banerjee (93) have reported the following dissociation constants $K_2$ for the complexes $MAc^+$ at about 30°C., ($Ac^-$ = acetate). For $M^{+2} = Pb^{+2}$, $Co^{+2}$, $Mn^{+2}$, and $Ni^{+2}$; $10^3K_2 = 3.31$, 30.2, 60.3, and 75.9 respectively. The dissociation constant $K_1$ for $MAc_2$ was too large to be determined accurately except for $M^{+2} = Pb^{+2}$ and $Co^{+2}$ for which the authors find $31.2\times10^{-3}$, $260\times10^{-3}$, respectively. Values for $PbPr_2$ ($Pr^-$ = propionate) at 21°C. are reported as $K_1 = 51.1\times10^{-3}$, $K_2 = 4.57\times10^{-3}$, while $K_2$ for $PbFo^+$ ($Fo^-$ = formate) is $182\times10^{-3}$. The values $K_1 = 22.5\times10^{-3}$, $K_2 = 43.5\times10^{-3}$ for $NiAc_2$ at 20°C. obtained spectrophotometrically by Watelle-Marion (94) are in poor agreement with the above. Dissociation constants of $4\times10^{-3}$ for $CdNO_2^+$ at 25°C. by Vassian & Eberhardt (95), and $2\times10^{-10}$ and $6\times10^{-7}$ for $Cd(OH)_4^{-2}$ and $Cd(CO_3)_3^{-4}$, respectively, (to free $Cd^{+2}$) by Lake & Goodings (96) have been published.

The following formation constants have been reported: the first through fourth for $Ag^+$ with anions of 11 sulfonated phenyl ethers, thioethers, selenoethers, amines, phosphines, and arsines at 25°C. by Ahrland & coworkers (97); antilogs of 33.9 for $Hg(CN)_2$, 38.1 for $Hg(CN)_3^-$, 40.6 for $Hg(CN)_4^{-2}$ (all from $Hg^{+2}$) by Newman, Cabral & Hume (98) polarographically at 30°C. and ionic strength 2.0 *M;* 7.2 for $TlS_2O_3^-$, 5.2 for $Tl(S_2O_3)_2^{-3}$, 1.5 for $Tl(S_2O_3)_3^{-5}$ (all from $Tl^+$) by Nilsson (99) using two methods at 25°C. and ionic strength 4 *M;* the first through fourth (from $M^{+3}$) for acetate complexes of $La^{+3}$, $Ce^{+3}$, $Nd^{+3}$, and $Gd^{+3}$ by Sonesson (100) potentiometrically at 20°C. and ionic strength 2 *M;* $5\times10^{12}$ for $Ag(S_2O_3)_2^{-3}$, $3\times10^{13}$ for $Ag(S_2O_3)_3^{-5}$, $2\times10^{26}$ for $Ag_2(S_2O_3)_4^{-6}$ by Nilsson (101) by two methods at 25°C. and ionic strength 4 *M*.

Using Kielland's (102) values for individual ion activity coefficients, Treumann & Ferris (103) have simultaneously determined 0.5745 ± 0.0002 v. for E° of the cell $Cd\text{-}Hg\,|\,CdCl_2(M)\,|\,AgCl\,|\,Ag$ and 90 ± 4 for the stability constant of $CdCl^+$ at 25°C. Using the emf. method of Harned & Ehlers (104), Treumann & Ferris (105) report a stability constant of $2.3\times10^5$ for $CdCit^-$ ($Cit^{-3}$ = citrate) at 25°C. Values for the molal stability constant of $Br_3^-$ at ionic strength 0.5 molal are reported by Scaife & Tyrrell (106) to be 19.8,

16.5, and 15.3 at 5°C., 25°C., and 35°C., respectively. Using this equilibrium as an indicator in a novel fashion, the authors (107) give the following values for the molal complexity constants (starting from $HgBr_2$) of $HgBr_3^-$: $230 \pm 25$ at 5°C., $135 \pm 10$ at 25°C., and $110 \pm 20$ at 35°C.; and of $HgBr_4^{-2}$: $5900 \pm 600$ at 5°C., $3060 \pm 200$ at 25°C., and $2000 \pm 250$ at 35°C. The high pressure solubility of $Li_2CO_3$ in $H_2CO_3$ solutions at 200°C. to 290°C. measured by Marshall, Loprest & Secoy (108) is consistent with the assumption that only $Li^+$ and $HCO_3^-$ are present in appreciable concentration. In disagreement with the earlier suggestion of Greenwald (109), Halla & Van Tassel (110) have found no evidence for the existence of a complex between $HCO_3^-$ and either $Ca^{+2}$ or $Mg^{+2}$ in aqueous solutions at 28.4°C.

*Other thermodynamic functions.*—Papers concerning activity coefficients in aqueous solutions are outnumbered by reports concerning nonaqueous or mixed solvents. In the former category are the following.

For 26 I-II or II-I electrolytes, Guggenheim & Stokes (111) have calculated renormalization factors (differing from unity by 2 per cent or less) to be applied to "best" values of $\gamma$ previously given by Stokes (112). The method is based on the use of empirical equations for activity and osmotic coefficients containing the same two empirical constants and is checked with McLeod & Gordon's (113) activity coefficient data for $CaCl_2$. By treating new or previously measured diffusion coefficients in a previously described (114) manner, Harned & Shropshire (115) have obtained precise activity coefficients at 25°C. and concentrations below 0.02 *M* for $LiClO_4$, $KClO_4$, and the nitrates of all alkali metals except rubidium. New precise data on cells containing HCl in a KCl solution have been obtained by Harned & Gancy (116) and analyzed by McKay's method (117). At constant total molality, log $\gamma$ HCl varies linearly with molality of HCl, but log $\gamma$ KCl varies quadratically with molality of KCl. The oxidation-reduction potentials of the couples Fe(II)-Fe(III) and U(IV)-U(VI) in phosphoric acid solutions at 25°C. have been investigated by Marcus (118). Kerker & Espenscheid (119) have essentially confirmed the data of Mason & Culvern (120) on the emf. of concentration cells containing $H_2PO_4^-$ and $H_3PO_4$, but have derived by Kerker's (121) method an entirely different value of $\lambda_0$ $H_2PO_4^-$ disagreeing with the value obtained from conductance (120). The disparity is removed by postulating association to $H_4PO_4^+$ to the extent of 1.5 per cent in 0.001 *M* $H_3PO_4$. From measurements of the emf. developed in a centrifugal field by symmetrical cells containing $I_2$ and about 0.1 *M* LiI, RbI, or CsI, Ray, Beeson & Crandall (122) have obtained cation transference numbers in good agreement with those obtained by the moving boundary method.

Turning to nonaqueous solutions, Izmaĭlov & Ivanova (123) have found only qualitative agreement between the Stokes & Robinson (124) equation for activity coefficients and data on 8 I-I salts in formamide, 4 I-I salts in methanol, and 2 I-I salts in butanol. Using a cell with a calomel electrode, Schwabe & Ziegenbalg (125) have determined the activity coefficient of dilute HCl solutions in methanol-water mixtures of four different composi-

tions at 25°C. Malcolm & Parton (126) have failed to obtain consistent E° values for the cell Na| NaCl (*M*) methanol-water| AgCl-Ag if Åkerlöf's (127) values of $\gamma$ NaCl are used. Estimates of $\gamma$ from the parallelism of $\gamma$ NaCl and $\gamma$ HCl, using Oiwa's (128) $\gamma$ HCl data, give consistent E° values for two values of *M* and three temperatures and solvent compositions. By re-examining Harned & Fallon's (129) emf. data on cells containing NaOH and NaCl in 45 per cent dioxane-water at 25°C., Nash & Monk (130) have obtained a dissociation constant of 0.35 for NaOH under these conditions. Continuing their study in mixed solvents, Alexandrov & Izmaĭlov (131) report on the emf. of cells containing HCl in ethanol, butanol, and isobutanol, all with very small amounts of added water. From dynamic measurements of activities of solvent components, Grunwald & Bacarella (132) have calculated the change with solvent composition of the standard chemical potential of NaCl in a dioxane-water mixture by using thermodynamic relations derived for this purpose. The activity coefficient of NaCl in 50 weight per cent dioxane-water at 25°C. is presented as a four-term power series in (molality)$^{1/2}$; the significance of the coefficients is discussed. The procedure has been repeated by Baughman & Grunwald (133) for HCl and NaOH; the autoprotolysis constant of water determined in this way differs significantly from the value derived from potentiometry. Attention must be called to a notable 60-page report by Oiwa (134) on his electrochemical investigations of HCl in water-methanol and water-ethanol mixtures. Results are interpreted both thermodynamically and structurally.

Combining free energies of formation of amalgams with their experimental data on the partition of metals between liquid ammonia and mercury, Schug & Friedman (135) report free energies of formation in liquid ammonia at 0°C. relative to $Na^+$ for: $K^+$, −3.1; $Rb^+$, −2.9; $Cs^+$, −5.6; $\frac{1}{2}$ $Sr^{+2}$, −5.4 (all in kcal./mole). For 47 salts, free energies of solution and related thermodynamic quantities have been calculated by Ladd & Lee (136) and compared with solubility data. Clever & Verhoek (137) have measured the solubilities of the iodates and the DL-dinitrooxalatodiammine cobaltates of *cis*- and *trans*-dinitrotetrammine-cobalt (III) at 15°C. and 25°C. in mixtures of water with dioxane, ethanol, and acetone. Heats, free energies, and entropies of solution are calculated.

Using essentially the same model of a hydrated ion as Levine & Wrigley (20), Buckingham (138) has calculated heats of hydration of ions. The effect of dielectric saturation outside the first shell is shown to be quite unimportant. The unknown quadrupole moment of water, numerically unimportant in Levine & Wrigley's calculation, here creates the difference in heats of hydration between oppositely charged ions. It is in fact thus evaluated from Verwey's (139) values for $K^+$ and $F^-$, a procedure perhaps not free from objections. The resulting standard heats of hydration for alkali metal ions and halide ions are systematically about $1\times10^{-12}$ erg/ion larger than Verwey's values, which would result in an error of roughly 15 per cent in the observable heat of hydration of an alkali halide. Bucking-

ham's values for the individual ions are about 20 per cent larger than the individual ion values calculated by a rather different method by Lagunov (140), whose derived values for all alkali halides agree with Mishchenko's (141) data within a few per cent.

The following precise experimental work is noteworthy. Young, Wu & Krawetz (142) have extended the measurements of Young & Smith (143) on the heat of mixing of solutions of two different salts to give final solutions of constant total molality. The heats of mixing vary quadratically with mole fraction of either solute. By using common anions, interactions of cations (at least one of which is small) are found to be relatively large. From measured specific heats of 0.5 to 3.0 molal aqueous HCl and NaOH over a temperature range of 0°C. to 130°C., Ackermann (34) reports the dissociation constant of water and partial molal entropies and heat capacities of the ions. Kirkbride & Wyatt (144) have measured partial molar heat contents of several bisulfates, acetic acid, and water in sulfuric acid at 25°C. The data supports the existence of both autoprotolysis and ionic dehydration, suggested earlier by Gillespie, Hughes & Ingold (145); molal dissociation constants, $3.4\times10^{-4}$ and $1.8\times10^{-4}$, respectively, and other thermodynamic functions are in good agreement with earlier cryoscopic work.

Heats of neutralization of benzoic acid and the four lowest alkanoic acids have been measured by Canady, Papée & Laidler (146). The following have also been reported: the heat of solution of $PuCl_3$ in various perchlorate solutions and approximate thermodynamic data for the dissociation of $PuCl^{+2}$ by Martin & White (147); partial molal heat capacities and relative partial molal heat contents of both components of aqueous phosphoric acid by Egan, Luff & Wakefield (148); a heat of formation of $-115$ kcal./mole for aqueous $FeO_4^{-2}$ by Wood (149). Entropies of 19 polyatomic anions (in the hypothetical gaseous state) have been calculated by Altshuller (150), who then obtains entropies of hydration wherever possible.

Although it cannot be discussed here, attention is called to deBethune's (151) paper on absolute electrode potentials.

*Miscellany.*—Reviews have appeared by Kraus (152) concerning the qualitative physical significance of a variety of properties of solutions of electrolytes, and by Schwarzenbach (153) concerning the chemical species present in aqueous solutions of metal salts. In extremely thorough fashion (33 tables and 196 references), Fischer, Winkler & Jander (154) have reviewed recent electrochemistry in nonaqueous solutions. Redlich & Hood (155) have presented an excellent discussion of ionic interaction, dissociation, and molecular structure. Though dealing directly with strong acids, there are widespread implications.

The nature of the chemical species present in solutions of cupric salts of alkanoic acids $H(CH_2)_nCO_2H$ (hereafter specified by n) has been extensively investigated. Magnetic susceptibility measurements indicate to Kondo & Kubo (156) Cu-Cu bonded dimers for $n=1$ in ethanol and dioxane. Similar results for $n=0$, 1, 2, 3, 4, 11, 17, and 21 in dioxane and benzene

indicate to Martin & Whitley (157) intramolecular exchange interaction within a binuclear complex. The latter group adduces conductivity and cryoscopic data and finds the "dimer" band spectroscopically. This band has been reported in solid salts and ethanolic solutions of n = 3, *iso*-3, 4, *iso*-4, 5, and 7, and acetic anhydride solutions of n = 15 and 17 by Yamada, Nakamura & Tsuchida (158), who discuss the dimer structure. The same group (159) has reported the band present in crystals and dioxane solutions of monochloroacetate and dichloroacetate, but absent for trichloroacetate. Dimers are apparently absent in pyridine (156) and water (156, 157). The formate is quantitatively anomalous (157) while methanolic acetate data (156) is unexplained.

Having found no spectroscopic evidence for either $H_2SO_3$ molecules or strong $SO_2$-water interaction even in solid solutions at −190°C., Falk & Giguère (160) have concluded that sulfurous acid is merely a convenient fiction. By contrast, they (161) have confirmed $OSe(OH)_2$, and have found no trace of either the unsymmetrical structure previously reported by Venkateswaran (162) or of $SeO_2$. Spectroscopic investigations of solutions of $HNO_2$ in $HClO_4$ have been reported by Bunton & Stedman (163) and by Turney & Wright (164), who have reported 51 kcal./mole as the standard free energy of formation of $NO^+$. Waggener (165) has made a preliminary report on the spectrum of the neptunium (V) ion in a $DNO_3$-$D_2O$ mixture at temperatures up to 252°C. A perturbation method for the calculation of the vibrational frequency of water in complexes has been presented by Furlani (166) and Sartori & Furlani (167).

The apparent molar volumes and refractions of aqueous nitrates of $La^{+3}$, $Ce^{+3}$, and $Nd^{+3}$ at 25°C. have been reported by Leipziger & Roberts (168). Joshi & Joshi (169) have noted an irregularity in the temperature variation of the refractive index of aqueous $Na_2SO_4$ at 37°C., in addition to the known irregularity at 32°C. Elamayem, Halim & Sadek (170) have determined equilibrium constants of 0.036 and 0.032 for proton transfer from HCl to mannitol and urea, respectively, and an over-all mean value of the energy of proton transfer in very good agreement with Gurney's (171) value. By various techniques, Flowers & his collaborators (172) have obtained values for the freezing point, cryoscopic constant, specific conductance, and density of $D_2SO_4$. Equilibrium constants are reported for the reaction of $D_2SO_4$ with $D_2O$, $SO_3$, and *m*-nitrotoluene.

Reports concerning some interesting and unusual electrolyte-solvent systems are largely of a preliminary nature. Jander & Günther (173) have measured conductances and van't Hoff factors for electrolytes [e.g., $AlCl_3$ and $(CH_3)_4NBr$] in molten $AsBr_3$. Jander & Weis (174) have discussed the behavior of many electrolytes in molten $SbBr_3$; Spandau & Hattwig (175) have reported a number of electrolytes (e.g., $SbCl_5$, $POCl_3$, and HCl) in $SnCl_4$. A stimulating cryoscopic study of KCl, CsCl, $(CH_3)_4NCl$, and triphenylmethyl chloride in molten $SbCl_3$ has been made by Porter & Baughan

(176). The first two compounds behave as weak electrolytes; the Debye-Hückel distance of closest approach obtained by fitting the osmotic coefficient data is less than the Bjerrum association distance (7.3 A) and is improbably small (2.1 A) for KCl. The last two compounds are strong electrolytes. In $CH_3NO_2$ solutions of triphenylmethyl chloride, the hitherto unsuspected presence of HCl and the effect of added $Cl^-$ are partially explained by Pocker (177) without recourse to ion-pair formation suggested previously by Evans *et al.* (178). In $CH_3CN$ solution, half-times for Cl exchange between dissolved $(C_2H_5)_4NCl$ and the ions $PCl_4^+$ and $PCl_6^-$ have been reported by Kolditz & Hass (179) as 1 to 19 min. (0.3 *N* to 0.01 *N*) and less than 0.6 sec., respectively.

### Nonequilibrium Properties

*Theory.*—By generalizing the equations of absolute reaction rate theory to multicomponent systems, Podolsky (180) has correlated fluidities of solutions, the self-diffusion coefficient of water in solutions, and limiting ionic mobilities. The usual free energy of activation is replaced by a sum over the types of particles entering that particular rate process, weighted by the fraction of particles of that type. The lattice model of an ionic solution appears in the specification of types present, namely free water, water in the solvation shell of each kind of ion, and each kind of ion. By expressing the free energy of activation for each type as that for self-diffusion of water plus a change, the expression for the relative fluidity contains only a particular combination of changes and hydration numbers. These are partially evaluated in terms of the individual ionic contributions $B_i$ to the coefficient $B$ of the Jones & Dole (181) relation for the relative fluidity. From the fact that over 30 ions fall approximately on a straight line (three do not) on a log mobility versus $B_i$ plot, it is inferred that a certain ratio of changes is independent of the ionic species and its value is fixed. Effective hydration numbers are not separately obtained, but the expression for the relative change in the self-diffusion coefficient is thereby uniquely determined as a function of $B$ and concentration. The predicted variation with $B$ agrees very well with Wang's (182) scanty data. Pressure and temperature effects are also discussed. Certain points, including some of self-consistency, are not carefully examined; but the correlation obtained is rather impressive.

Haase (183) has clarified the concepts used in his two earlier papers (184) on the interrelations of transport properties of ionic solutions.

*Conductance.*—A revision of the recently published conductance equations of Fuoss & co-workers (185, 186) has been announced by Fuoss (187); a procedure for the practical analysis of conductance data incorporating the revisions is presented. The derivation of the additional term linear in $c$ arising from the asymmetry of the perturbed ionic atmosphere has subsequently been published by Fuoss & Onsager (188). Šalamon (189) has described a novel electrodeless low frequency conductance apparatus in which

two transformers are coupled by a loop of solution. Graham & Maass (190) have developed a direct current conductance method employing an electrometer as a null indicator which is capable of high accuracy.

The following work in very dilute aqueous solution has been reported. Cappellina & Lorenzelli (191) have found $\lambda_0 = 36.15$ for $Fe(CH_3NC)_6^{+2}$ at 25°C. Unlike the value $\lambda_0 \simeq 92$ for this ion reported earlier by Hölzl (192), the new value leads to a reasonable ionic dimension. Campbell & Bock (193) have made careful conductance measurements on aqueous $NH_4Cl$, $NH_4Br$, and $NH_4NO_3$ at 35°C. From $\Lambda_0$ values obtained by Shedlovsky's (194) method (after correcting for hydrolysis) with Gordon & Benson's (195) $\lambda_0$ values for $Cl^-$ and $Br^-$, they obtain 88.73 and 84.48 for $\lambda_0$ of $NH_4^+$ and $NO_3^-$, respectively. These data and earlier data of Campbell, Gray & Kartzmark (196) on concentrated $NH_4NO_3$ solutions are better fitted by the Wishaw & Stokes (197) equation with $a = 3.0$ A than by the Falkenhagen & Leist (198) equation with $a = 2.3$ A. A Kohlrausch plot of Campbell & Bock's (199) data on very dilute $KIO_3$ at 25°C. leads to $\lambda_0\ IO_3^- = 40.91$. Bordi (200) has measured the surface tension and the surface conductivity of extremely dilute aqueous $MgSO_4$ and $CsNO_3$ at 25°C. An anomalous minimum in the surface conductivity as a function of concentration is found for both salts at about $5 \times 10^{-4}$ *M*, where the surface tension also has a minimum, an effect found earlier by Jones & Ray (201).

The following work on concentrated aqueous solutions has appeared. The practicality of a novel conductance apparatus having "noncontacting" electrodes previously described (202) has been tested on seven salts by Calvert & associates (203). Campbell, Kartzmark & Sherwood (204) have measured the density, viscosity, and equivalent conductance of aqueous $LiNO_3$ at 35°C., and of solutions equimolar in any two of $AgNO_3$, $NH_4NO_3$, and $LiNO_3$ at 25°C. and 35°C. Compared to the mean of solutions of the component salts alone at the same total concentration, the equivalent conductance for the mixed solutions were lower in all cases, and viscosities were lower in all cases but one. Campbell & Paterson (205) have measured conductances, densities, and viscosities of aqueous $LiClO_3$ up to 100 per cent $LiClO_3$ at 131.8°C., and to supersaturation at 25°C. The specific conductance shows a maximum at about 5 *M* at both temperatures; the equivalent conductance shows no minimum. At 25°C., there is very good agreement with a privately communicated revision of the Falkenhagen-Leist conductance equation, modified by the usual viscosity correction. Chambers (206) has accurately determined $\Lambda$ for aqueous KI at 25°C. and KCl and NaCl at 50°C.; interpolated values for round molarities above 0.05 *M* are also tabulated.

Stokes & Stokes (207) have reported $\Lambda_0$ at 25°C. in aqueous sucrose solutions of the following compositions: 10 and 20 per cent, for HCl and six salts including some II-I and III-I salts; 40 per cent, for HCl and KCl; and 60 per cent, for KCl. In 10 per cent aqueous mannitol at 25°C., $\Lambda_0$ is reported for eight I-I salts and HCl. Walden's rule is not obeyed in con-

centrated sucrose solutions. The ratio $\Lambda_0$ (solvent)/$\Lambda_0$ (water) does vary among the electrolytes considered here, in contrast with those previously considered (208).

Increasing interest in mixed and nonaqueous solvents is reflected by the following work in very dilute solutions. Dawson, Lester & Sears (209) have measured the equivalent conductance of N-methylacetamide solutions of 20 alkaline earth salts at 40°C. Using previously determined (210) anionic $\lambda_0$'s, they obtain good agreement between $\Lambda_0$ values determined by Onsager's (211) equation and by Shedlovsky's (194) modification, and derive 10.4, 10.2, 10.1, and 9.8 for the value of $\lambda_0$ for $Sr^{+2}$, $Ca^{+2}$, $Ba^{+2}$, and $Mg^{+2}$, respectively. El-Aggan, Bradley & Wardlaw (212) have measured conductances of absolute ethanolic solutions of HCl, CsCl, $MgCl_2$, and $LaCl_3$, with, in some cases, added traces of water. Dissociation constants $8.23\times10^{-3}$ (for HCl) and $6.61\times10^{-3}$ (for CsCl) are derived by Fuoss' (213) early method, CsCl requiring unequal distances of closest approach in activity coefficient and Bjerrum (14) dissociation constant expressions. Though the data on $MgCl_2$ and $LaCl_3$ extend to $10^{-5}$ $M$, they are ambiguously interpretable. From conductance measurements of absolute ethanolic $AgNO_3$ solutions at 25°C., Kikindai (214) has obtained the dissociation constant by several methods. The preferred value, 0.0060 by Shedlovsky's (82) method is significantly higher than that derived from the data of Copley *et al.* (215). The temperature variation is reported as $-\log K=(7588.8/T)-51.96+0.09708\ T$. Nash & Monk (216) have measured the conductance of solutions of NaCl in 70 and 82 per cent dioxane-water mixtures at 25°C., 30°C., and 35°C. These data and previously published data on KCl and HCl in dioxane-water at 25°C. are analyzed by four methods including Davies' (217) early method and Fuoss' (185) recent one. The former yields smaller values for the dissociation constant than the latter, the disparity increasing with increasing dissociation constant. The conductance of tetraethylammonium picrate in water-ethanol mixtures of six compositions at 25°C., 35°C., and 45°C. has been measured by Whorton & Amis (218). At each temperature the derived $\Lambda_0$ has a minimum value at about 25 mole per cent ethanol. From careful conductance measurements at 25°C. Davies & Thomas (219) have determined $\Lambda_0$ and the ion-pair dissociation constant $K$ for $MgSO_4$ and $CoSO_4$ in ethanol-water mixtures (up to 50 per cent ethanol). In 50 per cent ethanol, $Zn(ClO_4)_2$ appears completely dissociated, $\Lambda_0=46.10$; $AgNO_3$ nearly so, $\Lambda_0=48.55$; $CoCl_2$ yields $\Lambda_0=45.30$ by Onsager's (211) method and an approximate p$K$ of 1.63 for the dissociation of $CoCl^+$; similarly $KBrO_3$ yields $\Lambda_0=47.40$ and p$K=1.216$. Walden's rule is not obeyed. The observed dependence of $K$ on dielectric constant agrees with the Bjerrum (14) theory in the case of $CoSO_4$ but not $MgSO_4$.

A few investigations of more concentrated solutions have been reported. Thomas & Maass (220) have used a direct current method to measure $\Lambda$ for solutions of alkali metal halides, $H_2SO_4$, $HNO_3$, and HF in $H_2O$-$H_2O_2$ mixed solvent over the entire solvent composition range. Seward (221) has measured

the equivalent conductance and viscosity at 91°C. of solutions of tetrabutylammonium picrate in anisole, nitrobenzene, and ethylene carbonate over the entire composition range. In anisole, a maximum is found in the $\Lambda$ vs. $M$ curve; in the two latter solvents, a minimum occurs in the $\Lambda\eta$ vs. $M$ curve.

Griffiths & Pearce (222) have interpreted the effect on conductance caused by the addition of small amounts of cyclopentadiene and dicyclopentadiene to acetone solutions of $AgClO_4$ as arising from the formation of a silver "sandwich" complex with the former and a 1:1 complex with the latter. The conductance of $AgClO_4$ in binary mixtures of acetone, cyclohexanone, and isobutanol, and in benzonitrile with added ethanol or water has been measured by Griffiths, Lawrence & Pearce (223) and discussed primarily in terms of preferential solvation. Kirby & Maass (224) have measured the decrease in conductivity on addition of small amounts of water to ethylene glycol solutions of $H_2SO_4$, $HNO_3$, and HCl. There is an increase in conductivity if methanol is used in place of water, or if an alkali halide is used in place of an acid. An explanation in terms of proton transfer is suggested.

Fuoss & co-authors (225) have presented preliminary data on the conductance of tetrabutylammonium tetraphenylboride in four organic solvents. Typical strong electrolyte behavior is shown even with a dielectric constant of 20. Using a modified Hittorf apparatus, Lee & Millen (226) have obtained transport numbers and ionic conductances for $NH_4^+$, $Na^+$, and $K^+$ in $HNO_3$ at $-10$°C. Transport numbers for $NO_2^+$ and $NO_3^-$ obtained from pure $HNO_3$ and $N_2O_5$ solutions indicate the absence of a chain-conduction mechanism in this solvent. The electrode reactions are reduction of $NO_2^+$ to $NO_2$ and oxidation of $NO_3^-$ to $NO_2^+$ and $O_2$.

*Transference numbers.*—Steel & Stokes (227) have described a modified Hittorf transference number apparatus for use with mixed solvents. Nichol, Dismukes & Alberty (228) have incorporated the weak electrolyte moving boundary equation into the theory of electrophoresis. Very good agreement is obtained with data on an aspartate-acetate-glutamate system. Fritz & Fuget (229) have confirmed earlier and less accurate data on the transference numbers of both ions of $CuSO_4$ using the moving boundary method. Wall & Berkowitz (230) have measured transference numbers of the cations of 0.02 $M$ KCl, KBr, NaCl, and $NH_4Cl$ at 25°C. and 1, 500, and 1000 atm. by the same method used earlier by Wall & Gill (231) for 0.1 $M$ NaCl, KCl, and HCl. Ramirez (232) has reported a slight enrichment of $Li^6$ by countercurrent electromigration in aqueous lithium acetate.

*Viscosity, diffusion, sound absorption, etc.*—The fractional change in viscosity, density, etc., can be represented as some power (the "true" exponent) of the fractional change in concentration. The advantages of presenting the "true" exponent as a function of concentration are discussed by Andrussow (233). Suryanarayana & Venkatesan have measured the viscosity of aqueous KCl (234) and NaCl (235) from 1 molal to saturation

at 30°C. to 55°C. With $\eta^*$ and $C^*$ being the ratios of viscosity and concentration to their saturation values, the empirical equation $\eta^* = A \exp(BC^*)$ fits the NaCl data with a temperature independent $B$, but attempts to fit the KCl data are abandoned.

An extensive review of thermal diffusion and thermoelectric effects in ionic solutions has been published by Agar (236).

An apparatus for determining single ion-diffusion coefficients with a precision of better than 0.2 per cent has been described by Mills & Godbole (237). Grün & Blatter (238) have presented a diffusion theorem much more general than the one forming the basis for the frit method of Wall *et al.* (239). The new theorem justifies the use of a frit of arbitrary shape. By estimating the necessary activity coefficients for nine ternary systems, Miller (240) has found that all but one system confirm the Onsager reciprocal relations for ternary diffusion within estimated experimental error. The equivalent radii of a number of organic molecules (including the lower alkanoic acids) obtained from diffusion coefficients in water and the Einstein-Stokes law have been reported by Rossi, Bianchi & Rossi (241) to be uniformly 0.95 A larger than the calculated mean radius of gyration. This relation is replaced by others for benzene solutions. Harned & Shropshire (242) have measured the diffusion coefficient of dilute KCl solutions in 0.25 $M$ aqueous sucrose at 25°C., and have calculated the molar activity coefficient of KCl in this solvent. The diffusion coefficients of phenol, *o*-, *m*-, and *p*-cresol in water over a concentration range 0 to 15 gm./l. and a temperature range of 20°C. –50°C. have been measured by Erdös & Nývlt (243) and correlated with the Einstein-Stokes law, the Arrhenius expression, and the relation from absolute reaction rate theory. The diffusion potential at the end of a KCl salt bridge has been investigated by Kahlweit (244).

Eigen (245) has discussed the application of relaxation spectrometry to the general problem of determining, separately, general and specific interactions in ionic solutions. In particular, the absorption of sound by solutions of II-II electrolytes is considered in some detail. The general phenomenological problem of the absorption and dispersion of sound in chemically reacting fluids has been treated theoretically by Mazo (246) in a form differing somewhat from the earlier treatment of Meixner (247). Neglecting the small diffusion effects and all internal relaxations, and retaining only terms linear in small quantities, viscothermal and chemical absorptions are shown to be additive. There are brief applications to the dissociation of water and of $MgSO_4$. Kor & Verma (248) have measured the ultrasonic absorption coefficient of aqueous $MnSO_4$. These data on the temperature and dielectric constant variation of the relaxation frequency at about 3 mc. are construed as supporting a dissociation $MnSO_4 = Mn^{+2} + SO_4^{-2}$. The principal differences from earlier work are the absence of a maximum in the forward specific reaction rate constant with decreasing dielectric constant, and an activation energy 1/10 of that found by Smithson & Litovitz (249). Subsequently, Verma (250) has postulated a modified

mechanism. Extensive measurements on aqueous butyric acid by White, Moule & Benson (251) have revealed a sharp absorption maximum at about the critical solution composition (still noticeable 40°C. above the critical solution temperature) which is attributed to equilibria among clusters. A second absorption maximum at about 50 mole per cent is not definitely interpreted.

Ultrasonic vibration potentials of aqueous CsCl solutions have been measured by Rutgers & Rigole (252). In such solutions, the existence of this infrequently investigated phenomenon was predicted by Debye (253). In the present investigation, an increase in the potential at high dilution has apparently led to the discovery that this phenomenon is shown by pure water, deuterium oxide, methyl alcohol, ethyl alcohol, isopropyl alcohol, heptane, and nitrobenzene, but not by benzene. No satisfactory explanation has been found.

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# SOLUTIONS OF NONELECTROLYTES[1]

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Until recently it seemed that 1958 would be more notable for excellent work on certain special systems than for powerful contributions to the general theory of solutions. But a paper by Buff & Schindler (1) has done something to redress the balance. Starting with the expansion of the excess chemical potential of one component of a binary solution in powers of the concentration of the other [Buff (2) and Buff & Brent (3)], the radial distribution functions which enter into the coefficients in this series are now treated by perturbation theory (which is carried out to the first and second orders for simple systems). More explicitly, the interatomic potentials which determine these distribution functions are treated as perturbed forms of that appropriate to the solvent species. First order theory leads to the first order conformal solution theory of Longuet-Higgins (4), involving terms which may be regarded as negligibly small. Ignoring these and comparable terms, Buff and Schindler show that to deal with the second order terms it is necessary either to approximate to triplet distribution-functions or to make a physically plausible assumption about the solute-solvent distribution function in the limit of zero concentration. Two such assumptions are considered, one of which leads to the cell-model formulae of Salsburg & Kirkwood (5), and the other to those of the two-fluid model of Prigogine & co-workers (6) and Scott (7). Evidence is given for preferring the second of these approximations.

Rather similar work, although carried less far, has simultaneously been published by Mazo (8). This starts from the more cumbersome expressions of Kirkwood & Buff (9). For classical solutions Mazo goes only as far as the first order terms. But for isotopic mixtures he proceeds to the second order, obtaining results closely related to those of Chester (10). Both papers are useful in tying up previously rather unrelated approaches to approximate solution theory.

But the reviewer would like to pin his most personal remarks to a paper by Rubin & Sundheim (11). This somewhat obscure paper deals with radial distribution functions in binary gaseous mixtures and discusses the problem of condensation in what is generally known as Born-Green theory. Since the present author was concerned with this problem when last actively working on solution theory, a brief comment on it may be permitted.

As is well known, the Born-Green theory for a simple fluid produces a nonlinear integral equation for the radial distribution function $g(r)$, which, after being linearised, can be solved by a Fourier-transform procedure. In more detail, if $g(r) = \exp\,[f(r) - \phi(r)/kT]$, where $\phi(r)$ is the interatomic

[1] The survey of the literature was completed in December, 1958.

potential, and we keep terms linear only in $f(r)$, then $f(r)$ is given by an integral, with respect to the variable $s$, of a function of $r$ and $s$ which has as denominator the expression

$$1 - n\epsilon\beta(s) \qquad 1.$$

in which $n = \rho(2\pi)^{3/2}$, $\rho$ being the density of the fluid; $\beta(s)$ is fixed by $\phi(r)$ and the temperature $T$; and $\epsilon$ is a parameter which to a first approximation is unity but more accurately is given by

$$\epsilon = 1 + (3C/2B)\rho. \qquad 2.$$

$B$ and $C$ are the second and third virial coefficients of the fluid system [Rushbrooke & Scoins (12)].

The generalisation of these equations to binary mixtures has already been given by several authors [Rushbrooke & Scoins (12), Fournet (13), Rushbrooke (14), McLellan & Alder (15), Ling (16)] and it is now well known (*a*) that the system of integral equations for the three distribution functions $g_{ij}(r)$ are mutually consistent only after linearisation, and (*b*) that the denominator 1. is now replaced by the expression (often written in determinantal form)

$$(1 - n_A\epsilon_{AA}\beta_{AA}(s))(1 - n_B\epsilon_{BB}\beta_{BB}(s)) - n_An_B\epsilon_{AB}^2\beta_{AB}^2(s). \qquad 3.$$

Up to this point the paper by Rubin & Sundheim adds nothing new. But the problem is "How do these equations reflect condensation or, indeed, phase-separation, in a binary fluid?"

For a simple fluid, it is generally supposed that, at a given temperature, i.e., given $\beta(s)$, condensation occurs when the density $\rho$ first reaches a value for which the expression 1. vanishes for real $s$ [see Green (17), and also Scoins (18)]. In fact, for a condensed phase, $\rho$ must be such that $(n\epsilon)^{-1}$ is less than the positive upper bound of the function $\beta(s)$. And for real atoms this maximum value of $\beta(s)$ certainly occurs at $s=0$ [Montroll & Mayer (19)]. In this case the condensation condition, obtained from the expressions 1. and 2., can be shown to be entirely equivalent to the equation

$$\left(\frac{\partial p}{\partial \rho}\right)_T = 0 \quad \text{where} \quad p = \rho kT[1 + B\rho + C\rho^2]. \qquad 4.$$

Clearly the vanishing of the determinantal expression 3. is equally important in determining the onset of phase changes in a binary mixture. If the writer understands Rubin & Sundheim correctly, they have approximated 3. by a quadratic expression in $s^2$ after evaluating the $\beta$-functions more or less appropriately to argon-neon mixtures; and, then for fixed concentration $\rho_A/\rho_B$, have varied the total density to find its value when their approximation to 3. first vanishes for real $s$. In this way they claim to have obtained qualitative agreement with condensation phenomena in gas mixtures [on which, see Rowlinson (20)].

It is a pity that more details have not been published; for it is not without significance that, if a relevant vanishing of the expression 3. occurs at

$s=0$ and we use the binary analogues of equation 2. for the $\epsilon$'s, we are simply working out the condition

$$\frac{\partial(\mu_A, \mu_B)}{\partial(\rho, x)} = 0, \qquad 5.$$

where $x$ denotes concentration; the chemical potentials $\mu_A$ and $\mu_B$ being derived from the virial expansion of a binary gas mixture curtailed after the third virial coefficients [Rushbrooke (14)]. Equation 5. certainly implies large density and concentration fluctuations [see Pearson & Rushbrooke (21)].

Thus a much more detailed study of the expression 3. would seem desirable (and the writer hopes to undertake this with Dr. A. E. Rodriguez). For, if the Born-Green theory has a real validity within the liquid state, it would seem that $s=0$ should not be the value of $s$ at which 3. vanishes, and, moreover, the theory should predict phase-separation as well as condensation in appropriate cases. Until these questions are settled, it is perhaps premature to discuss the bearing of the Born-Green theory of mixtures on such work as that of Buff and Schindler.

Longuet-Higgins (22), using a constant-pressure grand partition function [see Brown (23)], has discussed one-dimensional multicomponent mixtures with arbitrary nearest neighbour interactions $\phi_{ij}(r)$. The equation of state, given by the vanishing of a determinant, generalises that of the similar Ising problem (localised systems) given by Rushbrooke & Ursell (24), the factors $\exp(-w_{ij}/kT)$ of the Ising problem being replaced by

$$\int_0^\infty e^{-\phi_{ij}(r)+Pr]/kT} dr,$$

where $P$ is the external pressure. For binary mixtures this had previously been found by Prigogine & Lafleur (25), who proceeded to discuss the result in terms of concepts (frequencies of vibration, anharmonic terms) appropriate to a cell model. Instead of doing this, Longuet-Higgins derives formulae, appropriate to the excess thermodynamic functions of nearly ideal solutions, which have the form (e.g., excess entropy)

$$\Delta S = \sum_{i<j} \sum x_i x_j (2S_{ij} - S_{ii} - S_{jj})$$

where the $x$'s denote mole-fractions and $S_{ij}$, for example, is the molar entropy for a pure component having intermolecular potential $\phi_{ij}$: and expresses the hope that they may prove of more general application.

The reviewer feels that perhaps the one-dimensional problem with interactions not restricted to nearest neighbours may not in fact be as intractable as appears at first sight, for the work on the corresponding Ising problem was not restricted to nearest neighbour interactions (and phase changes were then found to be precluded for any finite range of interaction).

On the Ising problem itself, little work has been published during the year. Katsura (26) discusses power-series methods for the plane square lat-

tice, but contributes little that is new apart from an elegant method of pulling out the quasi-chemical approximation. Much more is known of these expansions [see, for instance, Münster (27)]. Bell (28) has discussed dilution effects in regular assemblies, dealing in particular with the effects of impurities on transition points in solids. See also Levitas & Lax (29).

A somewhat new theoretical problem, not unrelated to solution theory, has arisen in work on free-radical stabilization in condensed phases [Jackson & Montroll (30) and Golden (31)]. Some a priori probabilities for single, double, and triple clusters in perfect solutions published by Behringer (32) might find application in this connection.

This appears to exhaust the theoretical papers of rather general application concerned with equilibrium properties. Transport properties are discussed separately below. Meanwhile other equilibrium work, chiefly experimental, must be surveyed more systematically.

## Critical Phenomena

Murray & Mason (33) have continued work on coexistence phenomena in the critical region, unsuccessfully attempting to detect by light scattering a gravity-produced concentration gradient in the aniline-cyclohexane binary liquid system at temperatures just above the critical mixing temperature [an effect predicted by Yvon (34)]. They infer that the flat apex of the coexistence curve for this system [see Rowden & Rice (35)] is not gravity produced (as has been suggested for certain one-component, liquid-gas systems).

Wolff & Bersntorff (36) have determined the coexistence curve for the liquid system acetone-*n*-heptane, which has an upper consolute temperature at −27.6°C., the curve itself being very symmetrical about an approximately 50:50 composition. Using activity coefficients determined from vapour-pressure measurements on this system at 0°C. and 50°C. [Schäfer, Rall & Worth-Lindemann (37)], they succeed in predicting this coexistence curve fairly accurately; the curve is very flat-topped.

Lorentzen & Hansen (38) have examined the coexistence curves for triethylamine-water (lower critical point) and succonitrile-ethanol (upper critical point), confirming the van Laar-Guggenheim formula

$$\Delta T = c(\Delta x)^3$$

in both cases.

Turning to solid solutions however, Münster & Sagel (39) show that for the gold-nickel system the phase boundary is much flatter than that given by this formula and indeed, when reduced variables are used, coincides very closely with that previously found for the aluminium-zinc alloy [Münster & Sagel (40)]. Since the alloys have the same crystal structure, both properties follow of course from an Ising model treatment. [See also Münster & Sagel (41).]

Using the small-angle scattering technique of Guinier & Fournet (42),

the same authors [Münster & Sagel (43)] claim to have demonstrated critical opalescence in the aluminium-zinc solid solution at 0.5°C. above the critical mixing temperature.

## Solid Solutions

*Inert gases.*—Walling & Halsey (44) [see also Singleton & Halsey (45)] have measured the vapour pressure of solid argon-krypton solutions from 70–90°K. [See Heastie (46) for previous measurements on this system.] They find that the argon vapour pressure can be fitted, over the whole range of composition, by regular solution theory with $w = 320 - 1.7\ T$ cal.mole$^{-1}$. Both the energy and entropy parts of this interaction are approximately half the corresponding values required for the krypton-xenon system [Freeman & Halsey (47)]. The extrapolated critical temperature for phase-separation comes to $56 \pm 8$°K., rather higher than that predicted by Domb (48) from heats of sublimation (10–40°K.).

*Metals.*—Freedman & Nowick (49) have estimated entropies of solution from solid solubilities (available phase-boundary data for alloys) and have compared the values so obtained with values calculated from the theories of Zener (50) (elastic dilation) and Huntington, Shirn & Wajda (51) (which takes account also of local distortion of the frequency spectrum), to the advantage of the latter theory.

Heats of formation of $\alpha$-phase silver-cadmium alloys have been determined, using liquid tin calorimetry by Orr, Goldberg & Hultgren (52). Orani & Murphy report heats of formation of alloys of silver, gold, and copper in both solid (53) and liquid (54) states; the enthalpies of formation of the liquid alloys from liquids correspond to those of forming the solid alloys from solids. Kubaschewski (55) has determined calorimetrically the isoenthalpy diagram for the aluminium-nickel-titanium ternary system.

Argent & Wakeman (56) calculate thermodynamic functions for zinc in copper-zinc solid solutions from vapour-pressure measurements.

Activities of chromium in nickel-chromium alloys at 750° and 965°C. have been found electrometrically by Panish & co-authors (57).

Keller, Kanda & King (58) have studied the barium-lithium equilibrium system, liquid and solid states, over the entire composition range, finding evidence for an intermediate solid phase, $BaLi_4$.

## Solid-Gas Systems

The work by van der Waals (59) on the dissociation pressures of quinal clathrates has now been extended to the gas hydrates by Platteeuw & van der Waals (60). In the quinol clathrates, the metastable form of the solid, stabilized by the dissolved gas, consisted of a three-dimensional network containing roughly spherical holes, all alike. The pressure of the gas which can occupy these holes, in van der Waals's theory, was essentially given by a Langmuir adsorption equation (the holes for "adsorption" being arranged

three dimensionally). Incidentally, this aspect of the theory has now been confirmed experimentally, for the quinol-argon compound at 60°C.; the argon pressure is indeed related to the composition of the clathrate, according to a Langmuir isotherm [Platteeuw (61)].

The gas hydrates now studied, which are of type I as classified by von Stackelberg & Müller (62), differ from the quinol clathrates in containing cavities of two types, large and small. There are then two equations of the Langmuir type for the pressure, one for each kind of cavity. If there is equilibrium between the hydrate and ice, the difference ($\Delta\mu$) in chemical potential between the normal ice ($\alpha$) and the metastable modification ($\beta$) is given by a third equation, involving the equilibrium occupancies of the cavities. Thus if $\Delta\mu$ is known, the equilibrium occupancies and the pressure of the gas can be calculated. Fortunately, $\Delta\mu$ can be found from the known composition of bromine hydrate in equilibrium with ice, for in this case the bromine molecules are too large to enter the smaller cavities.

To complete the calculations, the partition function for an encaged molecule, which enters the Langmuir equation, must be calculated. Platteeuw and van der Waals have evaluated these partition functions by a Lennard-Jones and Devonshire treatment which involves one unknown parameter (relating to the force field near the cavity walls). This parameter is chosen to fit the observed dissociation pressure for argon; the pressures for krypton, xenon, methane (fairly), and carbon tetrafluoride are then very satisfactorily reproduced as are the heats of reaction accompanying the formation of the hydrates from liquid water and gas.

This excellent paper is in the spirit of the best of solution theory, and raises the interesting question of the occurrence of a neon hydrate at sufficiently high pressures. According to the present theory this would not occur; but, as the authors observe, multiple occupancy of the larger cavities is possible for neon atoms and would lead to increased stability.

The other solid-gas paper which should be mentioned is that on the palladium-hydrogen system by Schuldiner, Castellan & Hoare (63). They believe there is experimental evidence that the electrolytic method of charging the metal with hydrogen produces an alloy with a higher free-energy content than the gas-charged alloy.

## Liquid Mixtures

*Special systems.*—The work of McGlashan & Rastogi (64) on dioxan-chloroform mixtures deserves special mention. The vapour pressures and heats of mixing of dioxan (A) and chloroform (B) at 50°C. have been measured with great accuracy over the whole concentration range. To correct for gaseous imperfections it is necessary to use the law of corresponding states for dioxan. The data are interpreted satisfactorily by assuming the existence of four species, A, AB, $AB_2$, and B which mix ideally [Dolezalek's method, see Hildebrand & Scott (65)]. The equilibrium constants for the dissociative

equilibria $A+B \rightleftharpoons AB$ and $A+2B \rightleftharpoons AB_2$ are found to be 1.11 and 1.24, respectively.

The other system which has been studied in order to test a particular specialised theory is that of benzene-o-o′-ditolyl by Kortüm & Vogel (66). Here again vapour pressures and heats of mixing have been measured over the whole concentration range, at 35°C. These molecules are more nearly of the single-double type (ratio of molar volumes 2.06) than those of the much studied benzene-diphenyl system [see Guggenheim (67) and Holleman (68)], and the authors find better agreement with the quasi-chemical lattice theory of the type AA-B with interactions.

*Fluorocarbon solutions.*—The critical review of work on fluorocarbon-hydrocarbon mixtures by Scott (69), mentioned last year by Rowlinson (70), has now been published; and, in continuance of work in this field, Croll & Scott (71) have further examined the methane-carbontetrafluoride system, at lower temperatures than those of the investigation of Thorp & Scott (72). They find a critical solution temperature at 94.5°K., with mole-fraction of carbontetrafluoride 0.43. The eutectic temperature (84.5°K.) and volume change on mixing at 107°K. have also been measured.

Bedford & Dunlap (73) have investigated solubilities and volume changes attending mixing for the system perfluoro-*n*-hexane-*n*-hexane, over a range of temperatures, and infer a critical solution temperature at 22.65°, with mole-fraction 0.370 of fluorocarbon. Strong opalescence was observed 4–5° above the consolute temperature, and the phase-separation temperatures have been verified by a study of the coefficient of expansion as a function of temperature.

Shinoda & Hildebrand (74) have measured the solubility and entropy of solution of iodine in various fluorine compounds, including the tetraperfluorobutyric ester of pentaerythritol (partial molar volume 542 cc.) and a dichlorohexafluorobutene (partial molar volume 140 cc.). They find that the difference in entropy of solution between these two solvents is much better accounted for by regular solution theory than by a Flory-Huggins treatment, using volume fractions instead of mole fractions. For use in calculating the "entropy of expansion" term in regular solution theory, the same authors (75) have determined the partial molar volumes of iodine in 25 complexing and noncomplexing solvents (including three fluorocarbons). And the whole subject of violet (noncomplexing) solutions of iodine has been admirably surveyed by Hildebrand (76) in an article in honour of the late Sir Francis Simon.

The fluorobutyric ester mentioned above provides a large compact molecule ideally suited to tests of the entropy of solution of molecules very different in size, other than long-chain molecules: and Shinoda & Hildebrand (77) have further measured its solubility in trichloromethane and carbontetrachloride, finding critical temperatures and compositions again in better agreement with regular solution than Flory-Huggins (polymer) theory.

*Other liquid systems, nonpolar and polar.*—Cardinand (78), by considering the totally deuterated system, has continued the work of Timmermans & Poppe (79) showing that the upper consolute temperature of the water-phenol system increases linearly with deuteration.

Newman & Jackson (80) have determined the vapour pressures of isotopic hydrogen mixtures between 18°K. and 28°K. obtaining (dew-point) excess free-energies in good agreement with those calculated by Prigogine, Bingen & Bellemans (81).

Roof & Crawford (82) report that phenanthrene and isobutane show incomplete miscibility at 101°C., remarkable in a mixture of hydrocarbons.

Ellis & Johnson (83) find that uranium hexafluoride and chlorine trifluoride have a lower critical solution temperature in the range 67–75°C. (no azeotropes), whereas uranium hexafluoride and bromine pentafluoride show evidence of azeotrope formation.

Goates & Sullivan (84) have obtained activities and excess free-energies for the system water-*p*-dioxane.

Mikus & Lawler (85) discuss liquid-vapour equilibrium for the system nitrobenzene-*t*-butyl.

Finally, Rowlinson (86) has criticised the interpretation of Balescu (87) and Prigogine (88) of the excess free-energy of chloroform-carbontetrachloride mixtures on the grounds that they have confused energy and free-energy in an approximate partition function. He believes there is a substantial nonpolar contribution to the excess free-energy, as in carbontetrachloride-benzene mixtures.

*Corresponding states and congruent mixtures.*—Desmyter & van der Waals (89) have continued work [see van der Waals & Hermans (90)] on binary mixtures of *n*-alkanes differing in chain length, with a view to testing Brønsted's principle of congruence [see Koefoed (91)]. They have measured volume changes on mixing, at all concentrations, for six different binary mixtures in the temperature range 20°–50°C., and describe a convenient dilatometer for this purpose. The observed volume contractions are in accordance with Brønsted's principle applied to the pure components, and Hijmans (92) has further shown them to be mutually consistent on the same basis.

The work of Cutler & collaborators (93) on the compressibility of several high molecular weight liquid hydrocarbons, including two binary mixtures, is rather similar in emphasis.

On the more general forms of corresponding state theories, little has been published other than that already referred to. Rice (94) has presented further justification of his earlier work (95) in the light of criticisms by Salsburg (96). And King (97) has analysed phase-boundary data for 24 binary systems in accordance with a principle of corresponding states (although this appears to amount to little more than enlightened interpolation). See also Pitzer & Hultgren (98).

*Ternary systems.*—Francis (99) has presented data, some new and some old, concerning 7 aqueous and 36 nonaqueous ternary solutions of hydrogen

halides (not including hydrogen fluoride). Arnold & Washburn (100) present the ternary solubility curves for the system isoamyl alcohol-isopropyl alcohol-water.

### Solubility of Gases in Liquids

A critical review of the solubilities, entropies, and partial molar volumes for solutions of gases in nonpolar solvents has been given by Jolley & Hildebrand (101), who inter alia report partial molar volumes of hydrogen, deuterium, and argon in a variety of solvents [for the entropy of solution of argon, see Reeves & Hildebrand (102)]. They conclude that mole-fraction and not volume-fraction is principally operative in determining such entropies of solution. [See Hildebrand (76) for further comments.]

Measurements by Gjaldbaek & Niemann (103) on the solubilities of argon and ethane in perfluoro-*n*-heptane and carbon disulphide both confirm and augment the data summarised by Jolley and Hildebrand. Gjaldbaek & Niemann have also (104) measured the solubilities of these gases in some polar solvents (alcohols and water).

Clever, Saylor & Gross (105) have measured the solubilities of helium, neon, argon, krypton, and xenon in methylcyclohexane and perfluoromethylcyclohexane at three temperatures [see Clever *et al.* (106) for other solvents]. The inferred heats and entropies of solution are less in the fluorocarbon than in the hydrocarbon, but both fit the same Butler-Barclay plot within the limits of experimental error.

Karasz & Halsey (107) have measured the solubilities of helium and neon in liquid argon, over the temperature range 83.9–87.5°K., and have analysed the data by means of a modified Lennard-Jones and Devonshire treatment.

Other solubility measurements at more than one temperature are those of Clever [(108) xenon in some hydrocarbons] and Grimes, Smith & Watson [(109) inert gases in molten fluorides].

### Spectral Studies

Perhaps the most interesting spectroscopic study on mixtures has been that of Colpa & Ketelaar (110), who, investigating the pressure-induced rotational absorption spectrum of hydrogen, report for a hydrogen-carbon monoxide mixture, the simultaneous excitation of a vibration in the carbon monoxide and a rotation in the hydrogen. The same authors have given a theoretical treatment of this effect (111).

The effect of pressure on spectra in liquid solutions has been investigated by Wiederkehr & Drickamer [(112) cyanide and carbonyl spectra in substituted methanes], and by Robertson & Reynolds [(113) $\alpha$-chloronaphthalene in ethyl iodide]. Robertson & Babb (114) have investigated the near ultraviolet absorption spectrum of benzene in carbon dioxide, ethylene, and ethane over a wide range of densities above and below the critical temperature.

Jefimenko & Gwinn (115) have studied the absorption spectrum of rubidium in isomeric hydrocarbon solvents.

Coburn & Grunwald (116) have made new infrared measurements of the association of ethanol in carbontetrachloride, and find support of Niini's vapour-pressure data (117), in contrast to deductions from the infrared data of Hoffmann (118).

Jones & McLaren (119) discuss the infrared absorption spectra of sulphur dioxide and carbon dioxide in water.

Brown (120) correlates infrared data for benzonitriles in various solvents with reactivities in electrophilic processes.

Solvent effects on X-H stretching frequencies have been investigated by Bellamy, Hallam & Williams (121), and by Josien, Lasconbe & Leicknam (122).

In connection with charge-transfer complexes, Pullin & Pollock (123) have measured the infrared spectra of silver and lithium perchlorates in acetone, and Daash (124) that of antimony trichloride in benzene. Ferguson & Matsen (125), by discussing the breathing band of benzene, suggest that infrared enhancement can occur in symmetrical complexes. De Maine (126) has investigated the ultraviolet bands of ethanol-iodine and methanol-iodine solutions. In the microwave region, Nederbragt & Pelle (127) have determined the dielectric properties of iodine in benzene, *p*-xylene, and mesitylene.

Pitt & Smyth (128) have measured the dielectric relaxation times of anthrone, fluorenone, and phenanthrenequinone molecules (prolate ellipsoids) in benzene.

Blume (129) has determined electron-spin relaxation times in sodium-ammonia solutions.

Stephen (130) has discussed the effect of molecular interactions in solution on magnetic shielding constants (for the interpretation of nuclear magnetic resonance spectra).

## Transport Properties

*Thermodynamics.*—A very general discussion of the thermodynamics of steady conduction-diffusion-reaction states of multicomponent fluid systems has been given by Brown (131); and essentially the same problem, but for nonreacting systems and without invoking the Onsager realtions, has been treated by Bearman (132). Both papers are phenomenological in outlook.

Statistically, Bearman & Kirkwood (133) have generalised the work of Irving & Kirkwood (134) to multicomponent systems, obtaining transport equations which imply the validity of the isothermal Onsager relations.

Experimentally, Miller (135) has presented evidence for the validity of Onsager's relations in connection with diffusion in ternary liquid systems, mainly electrolytic, but not exclusively so.

*Thermal diffusion.*—Saxena & Mason (136) have considered the second approximation in Kihara's scheme to the reduced thermal diffusion factor for isotopic mixtures [see Mason (137)] and have tabulated this for the (exp-6)

and (12-6) potentials and, for a smaller temperature range, for the Sutherland ($\infty$-6) potential.

Moran & Watson (138) have measured the thermal diffusion factor for the inert gases (from 230°–600°K.), finding values which agree well (except for helium) with those from viscosity data when the interatomic potential is represented by a modified Buckingham (exp-6) potential. The theory here is the second approximation in the Chapman-Cowling scheme [Mason (139)].

Srivastava (140) has tested his proposed combining rules (141) for this potential on the temperature and composition dependence of the thermal diffusion factor (using the first Kihara approximation); and he presents evidence that these rules are certainly no worse, indeed better as concerns the temperature dependence of the thermal diffusion factor, than the combining rules of Mason & Rice (142).

Walther & Drickamer (143) have measured thermal diffusion at high pressures in such gases as nitrogen, carbon dioxide, and ethylene, finding large negative values of the thermal diffusion ratio when one component is near its critical point.

*Thermal conductivity, viscosity, and self-diffusion.*—Using Kihara's approach, Mason (144) has shown how a formula much simpler than the Curtis-Hirschfelder formula for the thermal conductivity of multi-component gas mixtures, involving determinants of only half the order, can be derived with the same degree of rigour. [See also Muckerfuss & Curtis (145).] And with suitable approximations this simpler formula reduces to successful empirical equations. Brokaw (146) has dealt with much the same problem for thermal conductivity and viscosity, giving numerical comparisons of successive approximations. Francis (147) also has dealt with the viscosity equations for gas mixtures, proposing on theoretical grounds a relationship (for the viscosity of a mixture in terms of its components) which appears good to within about two per cent, even if one gas is polar. Madan (148) discusses the temperature variation of self diffusion, for xenon and neon, against (12-6) and (exp-6) potentials, with particular reference to the latter.

*Liquids and solids.*—Without a satisfactory theory of transport processes in condensed systems, theoretical work on liquids is still largely confined to pure substances. The admittedly over-simplified theory of Longuet-Higgins & Pople (149) has been extended by Valleau (150) to the case of rough hard spheres, who finds a thermal conductivity, $\lambda$, twice that for smooth spheres while the product, $D\eta$, of the coefficients of self-diffusion and shear viscosity is substantially unchanged. Longuet-Higgins & Valleau (151) have also extended this work to the case of smooth hard spheres surrounded by square-well potentials. They find $\lambda:\eta:\kappa = k/2:m/5:m/3$, exactly as for smooth hard spheres. Here $k$ is Boltzmann's constant, $m$ the mass of a system, and $\kappa$ the coefficient of bulk viscosity.

Now the temperature coefficients of $\lambda$ and $\eta$ are known to be very different, and it is clear that this simplified treatment of Longuet-Higgins and

Pople cannot give the proper temperature dependence of viscosity (crudely expressible in terms of an activation energy), certainly as long as it keeps to impulsive collisions. A very much more satisfactory theory, which for argon gives both the isobaric and isochoric temperature coefficients of the shear viscosity of the correct sign and of roughly the right order of magnitude, has been presented by Collins & Raffel (152). This is perhaps the most important paper for some time on transport processes in liquids, and is written with admirable lucidity. Space precludes an adequate discussion here, but the transport coefficients are finally expressed directly in terms of integrals over the equilibrium distribution function $g(r)$ and derivatives of the interatomic potential $\phi(r)$. It is interesting that this theory also gives $\eta : \kappa = 3 : 5$ (approximately), and again casts doubt on the supposition of classical hydrodynamics that $\kappa = 0$ [see Karum & Rosenhead (153)].

Hammond, Howard & McAllister (154) have measured the viscosities and densities of methanol-toluene solutions, at all concentrations, up to their normal boiling points.

Griest, Webb & Schiessler (155) have investigated the effect of pressure on the viscosities of higher hydrocarbons (25 or 26 carbon atoms) and their mixtures, finding a congruent mixture type of behaviour for the latter.

Toye & Jones (156) have measured the viscosity, density, and specific resistance of certain liquid alloys of tin and zinc, and infer the existence of short-range order well above the melting point.

Mackliet (157) has determined the activation energies for diffusion of iron, cobalt, and nickel in single crystals of pure copper, and discusses these against the background of Lazarus' screening theory (158). Hoffman (159) has studied diffusion in silver-germanium and silver-thallium solutions, and makes comparison with the theory of Hoffman, Turnbull & Hart (160), interrelating solvent and solute diffusivities.

The author regrets that this review is neither as complete nor as critical as he would wish, but has done his best to cover the field in the time available. Polymer solutions have been deliberately omitted. Russian literature has been very regretfully omitted owing to a combination of library and linguistic difficulties. And he tenders his apologies to writers whose work has been inadvertently overlooked or unintentionally misrepresented.

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# RADIATION CHEMISTRY[1,2]

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## INTRODUCTION

Radiation chemistry is the study of chemical effects produced by high energy radiation. The main problems include determination of the changes in chemical structure produced by radiation, investigation of factors influencing these changes, and elucidation of mechanisms by which changes take place. Applications of radiation chemistry in fields such as reactor technology and industry are important, and have been largely responsible for the rapid development of the subject; but this aspect is not dealt with here.

Recent review articles on Radiation Chemistry include the following: Lefort (1), in the 1958 edition of this series; Tipper *et al.*, in a review of recent work on chemical kinetics (2); Maurer, in a treatise on the fundamental aspects of radiobiology (3); Reid, in a discussion on the triplet state (4); Mohler, as editor of a book on radiation chemistry (5); and Haissinsky, as editor of a third volume on chemical and biological effects of radiation, including the chapters by Burton, Chapiro & Magat, and by Charlesby (6a). A collection of papers on radiation chemistry was published in the Soviet Union (6b). Radiation chemistry was discussed at several conferences. The most important were the *Second United Nations International Conference on the Peaceful Uses of Atomic Energy*, held at Geneva in September 1958, and the *International Congress of Radiation Research*, held at Burlington in August 1958 (7). Most of the papers read will be published in due course. Sixteen of the papers presented at the Ottawa symposium on excited species held in September 1957 have now been published (8). The proceedings of the first Soviet colloquium on radiation chemistry held in Moscow in March 1957 have also appeared (9); the results presented at this colloquium have already been discussed by Lefort (1).

## GASES

### Primary and Secondary Processes

A basic assumption in radiation chemistry is that the primary ionisation produced by fast-charged particles is random. Lampe, Franklin & Field (10)

[1] The survey of literature was completed on 15 November, 1958.

[2] The following abbreviation will be used: LET (linear energy transfer)

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have measured the cross section for ionisation by 75 ev electrons of such varied substances as inert gases, inorganic gases, and hydrocarbons. They do not agree with the rules of Otvos & Stevenson for calculating cross sections (11) and find the ionisation cross section to be proportional to polarisability.

Laidler has presented theoretical considerations on the radiochemical excitation of hydrogen and water (12) and oxygen (13), but it is not easy to draw practical conclusions from this work. Burr has drawn correlations between peaks observed in the mass spectrometer and radiolytic data (14, 15). For example, in the mass spectrum of acetic acid, the species $COOH^+$ is twenty times as abundant as $CO_2^+$, suggesting that ionised acetic acid loses methyl radicals more readily than methane in a "molecular process." This is in agreement with work on the radiolysis of liquid $CH_3COOD$, the methane consisting of $CH_4$ rather than $CH_3D$. Burr also discusses ethane, benzene, and alcohols.

The study of reactions between ions and molecules in the mass spectrometer has been pursued vigorously. Stevenson & Schissler discussed their work on ion-molecule reactions (16), and Gioumousis & Stevenson have discussed the theory (17). It seems that the rate of the reactions is inversely proportional to mass. Hence, ion-molecule reactions are unlikely to be as important in the radiation chemistry of large molecules as of small molecules.

Stevenson has presented the case for ion-molecule reactions in radiation chemistry (18). These seem to be important in the gas phase, where for a gas at one atmosphere and a dose rate of 300 rads/sec., each molecule could undergo $10^8$ reactions before neutralisation (18). Lampe, Field & Franklin (19) have calculated that in ion-molecule reactions in liquid water the lifetime of $H_2O^+$ would be $1.6\times10^{-14}$ sec., so that the reaction $H_2O^+ + H_2O \rightarrow H_3O^+ + OH$ would be likely to occur before neutralisation. Ion-molecule reactions are important because they explain how free radicals come to be formed.

Bardwell & his colleagues show the acceleration of the x-ray induced polymerisation of acetylene and ethylene by the addition of inert gases, especially argon (20). Lovelock measured low concentration of organic vapours ionised by collision with excited inert gases (21). Such energy transfer effects render it difficult if not impossible to prove the participation of sub-excitation electrons in radiation chemistry.

## Radiolysis of Gases

Organic compounds can be labelled by exposing them to tritium gas. Several new examples of this method have been described during the year (22, 23, 24). The method can be applied to solids, liquids, and gases; only solid surfaces become labelled. Free radical equations, such as $R + T_2 \rightarrow RT + T$, have been proposed but seem unlikely (22). The preferred mechanism is that ions formed from organic compounds react with tritium. Thompson &

Schaeffer even suggest that the radiation-induced exchange between hydrogen and deuterium is principally an ionic chain reaction (25). The $G$ value is about $10^5$, and can be reduced by xenon and krypton which have low ionisation potentials; argon, neon, and helium—gases with high ionisation potentials—have little effect.

Harteck & Dondes have discussed the radiolysis of $CO_2$, $NO_2$, NO, and $N_2O$ (26), and have given (27) an explanation of the pressure changes in irradiated nitrogen-oxygen mixtures first observed in 1936. They associate the initial decrease with the formation of $N_2O_5$ which then decomposes thermally into $NO_2$ and oxygen. After this, $N_2O_5$ formation is not important, the main products being $NO_2$ and $N_2O$. Burtt & Kircher (28) have studied the x-ray-induced decomposition of nitrous oxide in an applied electric field. Their results broadly agree with those obtained with $\alpha$-particles.

The irradiation of hydrocarbon gases has been reviewed by Davison, who presents fresh data on propane (29). Iodine suppressed the formation of higher hydrocarbons from propane, showing that this normally occurs by free radical combination. Iodine had little effect on hydrogen or lower hydrocarbon yields; a tentative reaction scheme is given involving both excited and ionised molecules. In contrast, Meisels, Hamill & Williams (30) explain the radiolysis of methane in terms of formation of $CH_4^+$ and $CH_3^+$ in the mass spectrometer ratio. The steps involve ion-molecule and free radical reactions. Meisels, Hamill & Williams discuss the irradiation of mixtures of argon and methane; argon, methane, and iodine; and others.

Dorfman irradiated mixtures of $C_2H_6$ and $C_2D_6$ and found less $CD_3H$ than expected if methane arose from free radical reactions (31). He suggests the methane is formed by

$$C_2H_6 \rightarrow C_2H_5^+ + H_2 + H + e^-$$
$$C_2H_5^+ + C_2H_6 \rightarrow C_3H_5^+ + CH_4.$$

The first of these reactions, together with

$$C_2H_6 \rightarrow C_2H_4^+ + H_2 + e^-$$
$$C_2H_6 \rightarrow C_2H_2^+ + 2H_2 + e^-$$

may account for the "molecular" detachment of hydrogen from ethane.

Hydrocarbon reactions induced by radiation become chain reactions at sufficiently high temperatures. Lucchesi *et al.* have irradiated both gaseous and liquid hydrocarbons at temperatures up to 510°C. $G$ values of the order of $10^5$ to $10^6$ were obtained; the products resembled those obtainable by thermal cracking (32). Mikhailov *et al.* studied the irradiation of ethylene at temperatures up to 290°C. The principal products were acetylene and butane. Free radical processes were proposed (33).

The possibilities offered by the gas phase for study of basic mechanisms are being exploited. One of the present needs seems to be for more comparisons between radiolysis in the gas phase and in the condensed phases, so that the gas phase results can be carried over to other systems.

## WATER AND AQUEOUS SOLUTIONS

The accepted position on the radiation chemistry of these systems has been presented by Hart (34). Miller also, has reviewed the radiation chemistry of aqueous systems (35), and Haissinsky has given a briefer review (36).

### Primary Processes

It is generally accepted that the principal primary process in the radiolysis of aqueous systems is the splitting of water into hydrogen atoms and hydroxyl radicals, but the mechanism is obscure. Baxendale & Hughes (37) support the Lea-Gray-Platzman view that electrons ejected from water molecules react according to

$$e^- + H_2O \rightarrow H + OH^-$$

leaving the positive ions to give hydroxyl radicals; they base their argument on the isotope effects found in the radiolysis of $H_2O - D_2O$ mixtures and conclude that fractionation must arise because of differences in activation energies for the reactions

$$H_2O^- \rightarrow H + OH^-, \quad \text{and} \quad HDO^- \rightarrow D + OH^-.$$

For many purposes it is unnecessary to know the mechanism by which radicals are formed, and it is sufficient to consider that the primary act is the formation of H and OH radicals together with molecular hydrogen and hydrogen peroxide. These substances are formed in constant yield for (*a*) radiation with a value of LET within a defined range, (*b*) solutions of given acidity, and (*c*) solute concentrations in the approximate range $10^{-4}$ to $10^{-2}$ *M*. Several recent determinations of the radical and molecular yields have been published (37 to 41). These are in reasonable agreement with previous determinations.

Regarding the effect of LET, Schuler has shown that for radiation of high LET, raising the concentration of ferrous sulphate from $2.5 \times 10^{-4} M$ to $10^{-2} M$ raises the ferric yield from $G = 4.01$ to $G = 4.38$. The yield is constant when $\gamma$-rays are used (42). Similarly Trumbore, using radiation of high LET, found for $3 \times 10^{-3} M$ ferrous sulphate solution that the oxidation yield rises from $G = 5.2$ in air-saturated solution to nearly 10 at oxygen concentrations above $10^{-1} M$ (43). Such effects confirm that competition between the reactions of free radicals with each other, with the molecular products, and with solutes in the bulk of the solution, is of increasing importance as LET increases. Pucheault has proposed a method for dealing quantitatively with this problem (44), and Flanders & Fricke (45) have calculated the fraction of radicals reacting with solute for a simplified system.

Low LET radiation at very high dose rates is like high LET radiation at low dose rates in that radical-radical reactions are enhanced at the expense of radical-solute reactions. Accordingly, Sutton & Rotblat, using a high energy pulsed electron beam, found an increase in molecular yield compared with free radical yield. The effect was strong for ceric sulphate (46). Hutchin-

son (47, 48) found similar effects with similar irradiation on $5\times10^{-6}M$ methylene blue. Dose-rate and concentration effects with dyestuffs have been noted previously (49) and have been interpreted in terms of competition between radical-radical and radical-molecule reactions (50), but such interpretations are not as valuable as hoped because of the complex radiation chemistry of dyestuffs.

Rothschild & Allen (51) using ferrous sulphate, and Baxendale & Hughes (37) using methanol as solute, confirm that H yield decreases as pH$>$1; molecular hydrogen shows a very small increase. Baxendale & Hughes suggest the equilibrium

$$H_2O^- \rightleftharpoons H + OH^-$$

which shifts to the right in acid solution. The species $H_2O^-$ is supposed not to attack methanol. However, with oxygen it might oxidise ferrous ions. Moreover, the yield of hydroxyl radicals is also higher in acid than in neutral solutions (52). Alternatively Horner & Swallow (53) and Swallow (54) found the yield of free radicals from pure cyclohexane to increase from $G=4.8$ to $G=7.0$ by addition of $0.23M$ hydrogen chloride. This is probably caused by transfer of excitation energy from cyclohexane to hydrogen chloride (see p. 299). It is suggested that the increase in the yield of free radicals from irradiated water from $G=4.8$ to $G=6.6$ by addition of $0.4M$ sulphuric acid (52) is caused by transfer of excitation energy from excited states of water which do not normally decompose, to the hydrated proton which then gives free radicals. This explains the equivalent increased yields of H and OH radicals. Phung & Burton's results (55) suggest the effect of acid on free radical yield from water is reduced when benzene is present since benzene may provide an energy sink.

Solute concentration studies provide important information about the primary act. Baxendale & Hughes (37, 39) found that cupric ions, ferric ions, and benzoquinone diminish the molecular yield of hydrogen. However, their effectiveness in this does not parallel that in reacting with hydrogen atoms. This shows there are other effects than that of scavenging free radicals; indeed, the solutes may capture electrons, which is indicated also by the aqueous methanol-metal ion system where ferric and cupric ions at concentration up to $5\times10^{-2}M$, can reduce the primary yield of hydrogen atoms while at the same time the reduction of metallic ions is slightly increased. This effect has been attributed to electron capture by the solute.

Studies of more concentrated solutions confirm scavenging of the precursors of the molecular yield, but also seem to show that excited water is present and active. Mahlman has shown that sodium sulphate up to $1.8M$ has no effect on the molecular hydrogen yield (56); but sodium nitrate (57, 58) decreases it appreciably and independently of radiation type. This is attributable to scavenging. In solutions above $1M$ the reduction of nitrate can become much greater than can be accounted for by the accepted yields for the radiolysis of water (59, 60). This implies transfer of excitation

energy from water to nitrate ions, as proposed for hydrated hydrogen ions. The irradiation of aqueous solutions containing ammonia and nitrate can also give very high nitrite yields, which imply the effective dissociation of nine water molecule per 100 ev absorbed (61).

We may conclude that the important primary process in the radiolysis of aqueous solutions up to $10^{-2}M$ is the production of H and OH radicals, some of which give "molecular products." The concentrated solutions electron capture by the solute and transfer of excitation energy also occur.

## Secondary Processes

There are two aims of work on secondary processes in radiation chemistry. The first is to establish the reaction mechanism for the system being considered. The second is to obtain quantitative data so that information can be carried over from one system to another.

*Ferrous sulphate.*—Acid aqueous solutions of ferrous sulphate or ferrous ammonium sulphate are the most thoroughly investigated systems in radiation chemistry. The reactions occurring when $0.1N$ or $0.8N$ sulphuric acid solutions are irradiated with x-rays or $\gamma$-rays are not well understood. When oxygen is present, ferrous ions become oxidised according to the equations

$$4.5H_2O \rightarrow 3.7H + 2.9OH + 0.4H_2 + 0.8H_2O_2 \quad 1.$$

$$H + O_2 \rightarrow HO_2 \quad 2.$$

$$HO_2 + Fe^{++} \rightarrow HO_2^- + Fe^{+3} \quad 3.$$

$$HO_2^- + H^+ \rightarrow H_2O_2 \quad 4.$$

$$H_2O_2 + Fe^{++} \rightarrow OH + OH^- + Fe^{+3} \quad 5.$$

$$OH + Fe^{++} \rightarrow OH^- + Fe^{+3} \quad 6.$$

In the absence of oxygen the system reaches an equilibrium, the position of which is governed by the rates of reactions 5, 6, and

$$H + H^+ + Fe^{++} \rightarrow H_2 + Fe^{+3} \quad 7.$$

$$H + Fe^{+3} \rightarrow H^+ + Fe^{++} \quad 8.$$

$$OH + H_2 \rightarrow H_2O + H \quad 9.$$

Several papers on these reactions have appeared recently. Allen & Rothschild studied the effect of oxygen concentration on the oxidation of ferrous ions in $0.8N$ sulphuric acid (62). They find the course of the reaction to be determined by competition of reactions 7 and 2. When little oxygen is present, reaction 8 can become important. These results confirm the predictions of the free radical theory. At higher pH values the same reactions occur, but differ quantitatively. On long irradiation at high pH the oxidation rate falls, because product ferric ions compete with ferrous ions for $HO_2$ (63).

Until this year, the reaction in air-free solution was less well understood. Rothschild & Allen (51) found the ratio of the rate constants for reactions 7 and 2 to be constant in the pH range 0.4 to 2.10 and conclude that reaction 7 occurs according to the equations:

$$H + H^+ \rightleftharpoons H_2^+ \qquad 10.$$

$$H_2^+ + Fe^{++} \rightarrow H_2 + Fe^{+3} \qquad 11.$$

the equilibrium in reaction 10 being to the right over the pH range studied. However, we prefer the alternative explanation that hydrogen atoms abstract hydrogen from the hydration shell of the ferrous ions

$$H + Fe^{++}\cdot(H_2O) \rightarrow H_2 + Fe^{+3}\cdot(OH^-) \qquad 12.$$

This explanation does not require $H_2^+$ to possess reducing properties nor to be capable of abstracting hydrogen from organic molecules, and agrees with recent evidence indicating that $H_2^+$ does not play an important part in radiation chemistry (see p. 296). Baxendale & Hughes found that the ratio of the rate constants for the reactions of hydrogen atoms with methanol and with ferrous ions is independent of pH (37) and also prefer to formulate the oxidation of ferrous ions as in equation 12. Czapski & Stein (64) and Hart *et al.* (65) have studied the oxidation of ferrous ions caused by free hydrogen atoms produced by the passage of an electrical discharge through hydrogen. The results are consistent with oxidation according to reaction 12.

Some years ago Proskurnin *et al.* reported the yield of ferrous ions oxidised could be as high as 63 per 100 ev absorbed. Western workers failed to confirm this. Ershler & Firsov have now shown that a ferrous ion-oxygen complex must be present in the solution for the effect to appear (66). The high yield is manifest only at the beginning of the irradiation. Spurny has also studied the reaction (67).

It is well known that many organic substances increase the rate of oxidation of ferrous ions when oxygen is present. Rösinger, Glocker & Goubeau have attempted to evaluate the contribution of each C-H group to the effect (68).

*Other aqueous systems.*—Koulkès-Pujo has studied in some detail the effect of chloride ions on the radiolysis of water (69). When oxygen is present, chloride decreases the hydrogen peroxide yield because it reacts with OH radicals, giving chlorine atoms. The chlorine atoms react with the $HO_2$ radicals which would otherwise give hydrogen peroxide and finally oxygen. Chloride is less effective in alkaline solution (70), and it was suggested that this is because hydroxyl radicals are present in the form of $O^-$ and cannot react with $Cl^-$. In the absence of oxygen, at pH O, the hydrogen peroxide yield is increased by chloride in the concentration range $10^{-2}$ to $10^{-3}M$, then decreased again in the range $10^{-2}$ to $1M$ (70). The maximum hydrogen peroxide yield is $G=0.36$, indicating that chloride ions are ineffective at capturing hydroxyl. Effects of pH were interpreted in terms of ionisation of the $HO_2$ and OH radicals.

Friedman & Zeltman have confirmed and extended other work on the conversion of *para*-hydrogen and on isotope exchange in solutions of hydrogen in water (71). They found the static hydrogen atom concentration in acid solutions to reach $2\times10^{-8}M$ at $10^{18}$ ev/1 sec., and the reaction

$$D + H_2O \rightarrow DOH + H$$

to be slow, with a *pseudo* unimolecular rate constant of 2 sec.$^{-1}$ at pH = 2. This implies at least one slow reaction in the sequence

$$D + H^+ \rightarrow HD^+$$

$$HD^+ \rightarrow H + D^+$$

$$D^+ + H_2O \rightarrow DOH + H^+.$$

In view of the ferrous sulphate considerations it seems likely the slow step is the first, hence $H_2^+$ is a much stronger acid than hitherto suspected.

McDuffie *et al.* (72) have studied the effect of catalysts on the reaction between oxygen and hydrogen (78). Cupric salts are effective at catalysing the reaction at 250°C.; the rate determining step is

$$Cu^{++} + H_2 \rightarrow CuH^+ + H^+.$$

Other catalysts tested were found to be less effective than cupric salts. Salts of noble metals were reduced to metals and initiated explosions. Haissinsky & Duflo studied the effect of heterogeneous catalysts such as cobalt sulphide, platinum black, and the oxides of tantalum, thorium, titanium, and niobium on the rate of various reactions. If oxygen is present, the rate can be increased threefold by the presence of a catalyst (73). Interpretation of these results is awaited with interest.

The effect of radiation on several inorganic systems has been studied in some detail. Simonoff found that permanganate becomes reduced on irradiation with $G$ up to 14.1 equivalents/100 ev (74). The irradiation product, even in acid solutions, is manganese dioxide. Lefort & Tarrago irradiated hydroxylamine. At pH-4 the main products are ammonium ions ($G = 2.25$) and nitrogen ($G = 2$). Hydroxylamine is lost with $G = 6.8$ (38). Daniels & Weiss irradiated aqueous arsenite (40). In alkaline solution the only product is arsenate; in acid solutions hydrogen peroxide is also formed.

Secondary processes in the radiation chemistry of dilute aqueous system can nearly always be interpreted in terms of simple free radical reactions. The principal need is for the determination of rate constants for the various reactions.

## Organic Compounds in Aqueous Solution

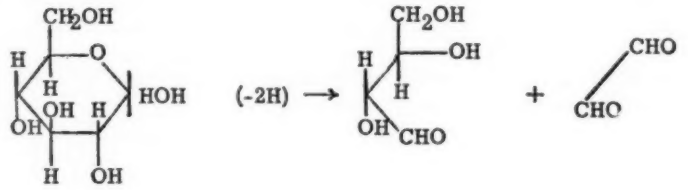
The primary aim in irradiating organic compounds is to determine the structural charges produced. It is also desirable quantitatively to establish the reaction mechanisms, but this must await the first result.

Clay, Johnson & Weiss have irradiated aqueous ethylene (75). In the absence of oxygen the principal products are aldehydes ($G = 0.24$ at pH = 1.2). The aldehyde yield increases several times when oxygen is present. Claims by previous workers that a chain reaction producing acetaldehyde occurred at pressures of the order of 10 atmospheres could not be confirmed.

Woods & Spinks extended earlier work to include bromal hydrate (76).

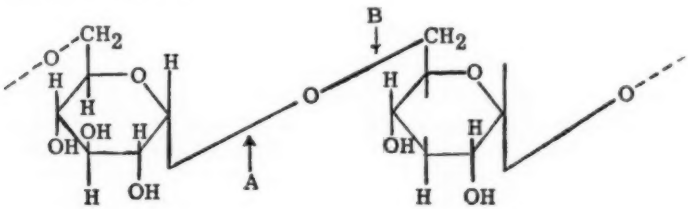
Hydrogen bromide and dibromo-acetaldehyde are the main products. The $G$ for HBr formation in the range 500 to 2500. Fenton's reagent initiates a similar reaction.

Some years ago Phillips claimed the irradiation product from hexoses was the corresponding uronic acid (77). Bothner-By & Balazs, however, could find no glucuronic acid from glucose (78). Phillips, Moody & Mattok (79) have now satisfactorily clarified the position. In aerated solutions the yield for loss of glucose is $G = 3.5$. The principal product is glyoxal, $G = 1.8$, formed partly together with erythrose by fission of the carbon-carbon bond between positions 2 and 3




The erythrose is attacked further giving more glyoxal. Glucuronic acid and its lactone is also a product. The absorption spectrum of irradiated solutions of glucose is associated with the formation of glyceraldehyde ($CH_2OH$ CHOH CHO), which isomerises to dihydroxyacetone, especially in alkaline solution.

Phillips & Moody extended this work to polysaccharides. The main primary attack on dextran when irradiated in aqueous solution can be represented as follows (80)




Attack at point A gives a gluconic acid unit (left) and a glucose unit (right). Attack at B gives a glucose unit (left) and an unstable dialdehyde which changes to a glucuronic acid unit (right). The irradiation of aqueous solutions of simpler ethers would be a valuable extension of this work.

Goodman & Steigman have found an ether-insoluble product from aqueous benzene irradiated in the presence of air (81), and Khenokh & Lapinskaya have found an ultraviolet-absorbing substance which is not produced by Fenton's reagent (82). Downes has studied the x- and γ-irradiation of aerated aqueous benzoic acid and salicylic acid. The main products from

benzoic acid are *o*-, *m*-, and *p*-hydroxybenzoic acids, formed with $G = 0.74$, 0.42, and 0.33, respectively. The yields differ somewhat from those reported previously.

The action of radiation on simple amino acids is now comparatively well understood. Weeks & Garrison have given a full reaction mechanism for glycine irradiated in air-free aqueous solution (83). This involves the formation of $CH_2COOH$ and $NH_2CHCOOH$ radicals. Small amounts of the corresponding dimerisation products were found. Rajewsky & Dose have shown that the yields from aqueous amino acids drops sharply when the solution is frozen (84, 85).

Kopoldová *et al.* (86), obtained further information on the radiolysis pattern of $S^{35}$-labelled methionine [$CH_3SCH_2CH_2CH(NH_2)COOH$]. The principal pathways are: deamination, decarboxylation, and attack at the sulphur atom. This latter can be reductive giving $CH_3SH$ and α-aminobutyric acid, or oxidative giving

$$CH_3SCH_2CH_2CH(NH_2)COOH \rightarrow CH_3SOCH_2CH_2CH(NH_2)COOH$$
$$\downarrow$$
$$HOSO_2CH_2CH_2CH(NH_2)COOH \leftarrow CH_3SO_2CH_2CH_2CH(NH_2)COOH.$$

Brdička and Spurný studied the kinetics of the oxidation of cystine to the disulphoxide (87); the highest yield found was $G = 5.02$. Vereshchinskii & Larin (88) found a yield up to $G = 20$ in the irradiation of sodium diethyldithiocarbamate.

Jayko & Garrison (89) found carbonyl groups in irradiated aqueous or solid proteins. Their presence is consistent with degradation according to the reaction.

$$R'CONH\ CR'' \rightarrow R'CON{=}CR'' \xrightarrow{H_2O} R'CONH_2 + O{=}CR''.$$

Confirmation of this reaction is possible by examining the damaged protein for amide groups. Engelhard *et al.* (90) discovered an effect of salt on the denaturation which could only be due to an effect on the stability of the protein. Magnan de Bornier irradiated trypsin (91); and found decreased affinity for the substrate (92). Yost *et al.* have shown that the substrate exerts a specific protective action on tyrosinase which cannot be attributed to competition for free radicals. The results indicate that tyrosinase has two sites of enzyme activity, a cresolase site and a catecholase site (93).

Fricke & colleagues studied the loss of serological activity in irradiated ovalbumin (94). Damage to some of the molecules results, but the undamaged fraction has undiminished serological activity. Sowinski *et al.* irradiated dry fibrinogen and demonstrated that both fragmentation and aggregation occurred (95), but were unable to decide whether the aggregates were cross-linked material or damaged protein molecules.

α, β, γ, δ-Tetraphenylporphine was shown by Szutka, Hazel & McNabb to be reversibly oxidized on irradiation in strongly acid solutions, reacting as with Fenton's reagent or ceric ions (96). Rothschild, Cosi & Myers find

that ferriprotoporphyrin gives the same product on irradiation in aerated aqueous solution as on treatment with hydrogen peroxide. Ring breakage, if it occurs, is a secondary reaction, but ferrideuteroporphyrin, a similar molecule, suffers ring breakage immediately (97). Tappel (98) has shown that the product absorbing near 608 mμ obtained by irradiating ferricytochrome-c is probably an oxyporphyrin.

A study of the radiation chemistry of air-free solutions of diphosphopyridine nucleotide ($\sim 10^{-3} M$) containing an excess of ethanol ($\sim 0.5 M$) was undertaken in the hope that the reactions would resemble those produced by alcohol dehydrogenase. This was not realized for Stein & Swallow (99) have shown that the reduction product is a dimer of the radicals first formed from diphosphopyridine nucleotide.

Irradiation of other nucleotides in the absence of ethanol gives different and much less specific results. Hems & Eidinoff found at least seven products from the irradiation of adenosine phosphate. From adenosine diphosphate, the principal product appears to be adenine itself (100). Guanosine monophosphate and guanine, in contrast, suffer attack on the imidazole ring (101).

Peacocke & Preston (103), have confirmed earlier work by Cox *et al.* (102) on the degradation and denaturation of deoxyribonucleic acid produced by irradiating it in aqueous solution with γ-rays. The most remarkable result is the high yield ($G = 50\text{-}60/100$ ev) for breakage of hydrogen bonds. The adenine-thymine bonds appear to be broken more readily than the guanine-cytosine bonds.

In conclusion, perhaps the most pressing need in aqueous organic radiation chemistry is for more studies of simple compounds to establish the response of particular groups to irradiation.

## ORGANIC LIQUIDS

### Primary and Secondary Processes

Burton has dealt with the radiation chemistry of organic liquids (6) and has called attention to some of the gaps in our present knowledge of the primary processes (104). Particularly important is the lack of knowledge concerning reactions of ions and excited molecules prior to their decomposition into free radical or molecular products. Burton & Lipsky reviewed this problem (105) and discussed four possible processes: transfer of positive charge, transfer of excitation energy, capture of electrons by the solute, and a quenching process by which an additive promotes the removal of excitation energy. It might be thought that fluorescence studies would be relevant to the transfer of excitation energy; it is not clear how this work bears on chemical effects.

Horner & Swallow irradiated $0.23 M$ solutions of hydrogen chloride in cyclohexane (53, 54) and found more hydrogen and more free radicals than from pure cyclohexane. The properties of the system are such that the results must be caused by either transfer of energy from excited cyclohexane, or

excitation of the HCl by subexcitation electrons produced from cyclohexane. Schuler studied the effect of solutes such as iodine, alkyl halides, and sulphur dioxide on the radiolysis of cyclohexane (106). The effects are attributed to electron capture by the solute, but transfer of excitation energy is equally probable. Schuler concludes that solutes cannot affect the primary processes unless they are present at concentrations greater than about $10^{-4}M$. Burton & colleagues discussed the effect of benzene and iodine on the primary processes in cyclohexane (107). All four processes discussed by Burton & Lipsky (105) can be operative in this complex system. Magat *et al.* (108) presented several cases where the yield of free radicals from binary systems is a non-linear function of composition. They interpret their results in terms of transfer of excitation energy. Energy transfer to substances which give free radicals such as benzoyl peroxide, azoisobutyronitrile (109), and tertiary butyl peroxide (110) has been studied by Krongauz & Bagdasaryan.

Sulphuric acid ($0.05M$) has been shown by Adams & Baxendale (111) to increase the yield of hydrogen atoms from irradiated liquid methanol from $G=2.4$ to $G=3.8$, while the yield of methyl radicals is reduced from $G=1.0$ to $G=0.2$. They suggest that in acid the ion $CH_3OH_2^+$ captures electrons to give hydrogen atoms, otherwise the electrons are captured by methanol giving methyl radicals. Meshitsuka & Burton studied the effect of solute, including iodine, on the radiolysis of methanol (112). Iodine is considered to interfere with the primary processes by capturing electrons.

Burr (113) finds the total hydrogen yield from irradiated ethanol to be reduced from $G\sim3.7$ to $\sim3.0$ when the hydrogen atoms in the $CH_2$ group are replaced by deuterium; substitution of other hydrogen atoms has no effect on yield. This indicates the main "primary" act to be

$$CH_3CH_2OH \rightarrow CH_3CHOH + H.$$

A high percentage of deuterium appears in the radiolytic gas when $CH_3CH_2OD$ is irradiated. This suggests as a secondary process

$$H + CH_3CH_2OH \rightarrow H_2 + CH_3CH_2O.$$

The $CH_3CH_2O$ radicals disproportionate giving acetaldehyde and ethanol. The $CH_3CHOH$ radicals disproportionate, but also dimerise giving glycol.

Schuler has discussed the use of scavengers for measuring radical yields (114). Collinson *et al.* have used ferric chloride as a scavenger to measure radical yields for a number of solvents (115). Their result for methanol, $G=6.3$, agrees with that obtained by Adams & Baxendale (111), but their results differ from previous results obtained with diphenylpicryl hydrazyl. Charlesby & Lloyd have studied the reaction of anthracene in cyclohexane and found both a concentration and dose-rate dependence in conformity with a theory assuming competition between radical-radical and radical-anthracene reactions (116). Dewhurst has used radical scavengers to help to decide on the origin of the products from *n*-hexane (117). Radical scavengers decrease the yields of hydrogen and "intermediate" and dimeric hydrocarbons, but not that of lower hydrocarbons.

Comparing the radiation chemistry of organic liquids with that of water it appears that there is much more awareness of the effect of solutes on the primary processes for organic liquids; but, where secondary processes are concerned, knowledge of aqueous systems is very much the more advanced.

## Structural Changes

Cyclohexane is one of the simplest organic compounds in its response to radiation, but Nixon & Thorpe appear to have found that besides dicyclohexyl and cyclohexane there is formed methyl-cyclopentane and dimers and polymers of cyclohexadiene (118). Dewhurst studied the *n*-alkanes; particularly *n*-hexane, and finds, contrary to previous belief, the ratio of C—C breaks to C—H breaks to be greater than if bond breakage were random (119). This conclusion agrees with the relative bond strengths. Further, there is preferential breaking of those bonds preferentially broken in the mass spectrometer, or which have less energy. Dewhurst also finds the yield of hydrogen from irradiated *n*-alkanes to be about $G = 4.5$ and independent of chain length from $C_5$ to $C_{16}$. Both Dewhurst (119) and Polak *et al.* (120) find that methane from *n*-alkanes decreases with the ratio of C—$CH_3$ to C—H groups. In *iso*-octane this effect is further reinforced by the weakness of the C—C bonds at the branch position. An extreme example of this effect was found by Hamashima, Reddy & Burton (121) who showed that liquid neopentane gave methane with $G = 3.18$ but hydrogen only with $G = 1.40$.

Polak *et al.* have also investigated the radiolysis of hydrocarbons by spectroscopic methods (122). Caffrey & Allen made an important observation on hydrocarbons which may be relevant to the question of the radiogenesis of petroleum (123). They find that when a thin layer of *n*-pentane on silica gel is irradiated there is an "energy transfer" so that its decomposition is enhanced, and the distribution of products is altered with less hydrogen appearing.

The oxidation of hydrocarbons and other substances under irradiation continues to attract attention in Russia. Emanuel *et al.* (124) report on the initiation, at elevated temperatures of the chain-oxidation of *iso*-decane. Bach & Saraeva (125) reported that the main oxidation products of *n*-heptane are carbonyl compounds.

The radiolysis of 1-hexene has been studied by Kharasch & colleagues (126). Little hydrogen is produced ($G = 0.8$) and the main products are dimers and higher polymers of hexene. The over-all yield for loss of hexene was $G = 10.5$.

Radiation-induced reactions of unsaturated hydrocarbons with other substances has been a popular field of study because of high product yield, possibly of practical significance. The reactions are similar to those induced by action of ultraviolet light or free-radicals, except that initiation is by a nearly random production of free radicals. Fontijn & Spinks studied addition of *n*-butyl mercaptan to 1-pentene (127, 128, 129). The only difference from the photoinitiated reaction was an apparently greater dependence of radiation-induced reaction on traces of impurities. El-Abbady & Anderson have studied

the addition of silicon hydrides to alkenes (130). Cox & Swallow reported on the bromination of cyclohexene with N-bromosuccinimide (131). Henglein, Url & Hoffmeister found that sulphur dioxide reacts with cyclohexene by a chain reaction, whereas with aliphatic or aromatic hydrocarbons it acts as a bivalent radical trap, giving in the first instance sulphinic acids (132).

Aliphatic or olefinic hydrocarbons are generally less stable to irradiation than aromatic hydrocarbons. Shida *et al.* however have found that *cyclo*-octatetrene, $C_8H_8$, although not possessing aromatic properties, is about as resistant as benzene (133). Gordon & colleagues have obtained important information on the nature of the polymer derived from benzene (134). The initial product contains biphenyl, phenylcyclohexadiene, phenylcyclohexene, and bicyclic nonaromatic compounds. It appears that the mechanisms previously accepted need revision, and Gordon *et al.* propose a tentative scheme. Feng & Mamula have shown that benzene-carbon tetrafluoride mixtures yield fluorobenzene and benzotrifluoride, and they argue that the reaction is not free radical in nature (135). The chlorination or bromination of aromatic compounds however are typical free radical chain reactions, and Cox & Swallow (131) and Rosen & Stallings (136) have shown that the products from toluene are identical with those obtainable in other ways. Cox & Swallow report the chlorination of benzyl chloride by irradiation, a reaction which previously had been thought impossible (131). Proskurnin & colleagues have called attention to the improved yields of phenol obtainable by irradiating benzene-water mixtures at temperatures up to 220°C., the yields being several times greater than from benzene or from benzene-water at lower temperatures (137).

Wiley *et al.* (138) discovered that irradiation of alkyl chlorides yields isomerisation products. These reactions appear to involve the rearrangement of free radical intermediates, e.g.,

$$CH_3CH_2CH_2\cdot \rightarrow CH_3\dot{C}HCH_3.$$

The irradiation of chloroform has been further studied (139). Futrell & Newton found the *cis* and *trans* isomers of 1-, 2-dichloroethylene oxide in irradiated 1-, 2-dichloroethylene which had been allowed to stand in the presence of air for some months, $G$ being up to 9 (140).

The radiolysis of ketones has been studied for the first time in any detail (141). Ausloos & Paulson show that liquid acetone, for example, gives methane, hydrogen, carbon monoxide, and ethane. Experiments with added diphenylpicryl hydrazyl and with deuterium enabled aspects of the reaction mechanism to be established.

The radiolysis of ethers was investigated by Newton (142, 143). Hydrogen is an important product, the yield decreasing with branching. Other products include hydrocarbons, alcohols, alkenes, carbonyls and probably dimers.

Tributyl phosphate on irradiation yields dibutyl phosphate, hydrocar-

bons, hydrogen, and a "polymer" (144, 145). *Tri*-isopropyl phosphite becomes oxidised by radiation when air is present, by a chain mechanism (146).

Isopropyl acetate is very different from butyl phosphates in response to irradiation (147). Isopropenyl acetate stands in the same relationship to isopropyl acetate as alkenes to alkanes in that gas production is much less, and "polymer" formation greater. The oxidation of fatty acid esters under irradiation is important in connection with the irradiation of foodstuffs (148). *Trans*-isomerisation of unsaturated fatty acids or their potassium salts (and presumably of their methyl esters) can also occur (149).

Schenck & colleagues have shown similarities between the radiation chemistry and photochemistry of the azodicarboxylic esters (150) and of diazoacetic ester (151).

## INORGANIC SOLIDS

Nitrates decompose into nitrite and oxygen on irradiation. The irradiation of calcium nitrate and its tetrahydrate has been studied by Baberkin & Proskurnin (152). Cunningham & Heal have irradiated a range of nitrates and find results in broad agreement with those reported previously by other workers (153). Silver nitrate is decomposed only in low yield because much of the radiation energy is absorbed in the silver ion. For other nitrates the order of increasing sensitivity to radiation is the same as the order of increasing free space in the crystal, i.e., $LiNO_3 < NaNO_3 < RbNO_3 < CaNO_3 < KNO_3$. Apparently oxygen atoms can escape recombination with nitrite when there is a large free space. Hall & Walton find that recoiling fission fragments decompose potassium nitrate with the high yield $G = 10.5$ for nitrite formed (154). They attribute the yield to the absence of a cage effect and to the fact that, because of the high temperature prevailing along the particle track, the oxygen atoms formed prefer to combine with each other rather than to react with nitrite to give nitrate. Johnson has found that the irradiation of lead nitrate is less simple than previously thought (155). Not only are nitrite and oxygen formed, but also lead oxide. The over-all reaction obtained after dissolving the irradiated crystals in water being as follows

$$Pb(NO_3)_2 + H_2O \rightarrow PbO + NO_2^- + NO_3^- + \tfrac{1}{2}O_2 + 2H^+.$$

Bowden has emphasized the remarkable stability of explosives under irradiation (156). Intense beams of electrons can cause explosion only because of the heat produced. Nitrogen iodide can be exploded by $\alpha$-particles because of the removal of a stabilizing film of ammonia from the surface. Thermal decomposition of the material can be enhanced, however, and the induction period for explosion reduced (157, 158). Lead styphnate, containing an aromatic ring, is the most radiation-resistant explosive (159).

Harbottle & Maddock found that the radiosensitivity of chromium compounds increases in the order: chromate < dichromate < trichromate < chromic anhydride (160). They suggest that sensitivity may be related to

the inherent density of defects in the crystals. Other studies of inorganic solids have been made by Hall (161) who reports the fission fragment-induced decomposition of uranyl iodate gives $G = 5.8$ iodine atoms formed per 100 ev absorbed, and by Jones (162) who finds that potassium bromide gives bromate when irradiated in the presence of oxygen but nitrate when irradiated in the presence of air.

## ORGANIC SOLIDS

Willard & colleagues reviewed the effect of phase in radiation chemistry, photochemistry, and radiochemistry with special reference to the alkyl halides, and have presented further data on the alkyl iodides (163). The characteristic feature of the solid state is that the free radicals produced are immobile so that reaction with solutes or with other radicals not produced in the same "cage" is hindered. An important consequence of this feature is that many of the radicals produced in solids have lifetimes long enough for them to be studied by ultraviolet spectroscopy and electron spin resonance. Shields & Gordy have studied further the electron spin resonance patterns given by irradiated amino acids (164). All amino acids which contain sulphur give similar patterns, so that the odd electrons may have been located on sulphur atoms. Similarly the patterns of tyrosine and tryptophan suggested that the free radical centres were in the benzene ring.

A tendency for radical centres to appear at sulphur atoms or benzene rings was also noted in work with peptides (165). The irradiation of caproamide and caprolactam (166) is also relevant to the effect of radiation on peptides. Norman & Ginoza obtained results indicating that intimate mixtures of substances such as cysteine and glutamic acid give electron spin resonance patterns which differ from those of coarse mixtures of the two substances (167). This might be because free radicals are formed from one substance at the expense of the other. It would be interesting to know whether the patterns of the individual compounds support this interpretation.

A disquieting feature of much of the work with the electron spin resonance technique is the poor agreement between the results obtained by different workers, and a concerted attack on one or two simple substances, such as glycine, would be valuable. Another difficulty is in the interpretation of the data. It was originally hoped that the electron spin resonance technique would permit the unambiguous identification of radicals and would help in explaining radiation-chemical data, but in a recent study the help has been in the reverse direction. Smaller & Matheson (168) concluded from work on the electron spin resonance of irradiated hydrocarbons and other substances, that a nonrandom breakage of C—H bonds was the main process responsible for free radical formation. Free hydrogen atoms were not generally found, although Cherniak *et al.* appeared to have detected hydrogen atoms in irradiated hydrocarbons (169). Smaller & Matheson found that little C—C rupture occurred except for branched hydrocarbons, perhaps be-

cause cage effects not operative in C—H breakage favoured recombination of the relatively large hydrocarbon radicals. In the case of methanol and ethanol the principal radicals formed were believed to be $CH_2OH$ and $CH_3CHOH$, rather than $CH_2^+$ and $C_2H_4^+$ as suggested by previous studies of electron spin resonance data.

The radiation decomposition of choline chloride,

$$(N(CH_3)_3CH_2CH_2OH)^+Cl^-$$

is unusual in that a chain reaction occurs in the solid phase. Lemmon *et al.* have studied the reaction further (170). The initial yield of free radicals as measured by electron spin resonance is $G = 0.01$, and reaction occurs over a period of several hours. The instability of choline chloride is a function of the crystal form. Choline chloride is decomposed in aqueous or ethanolic solution with $G$ values of only 2 to 4. In the solid phase there is less decomposition at 150°C. than at room temperature (171) and Collin has shown that this may be connected with the existence of a transition from an orthorhombic phase to a disordered cubic phase occurring at about 73–78°C. (172).

## POLYMERS

Research on the irradiation of polymers follows three main lines; the study of basic mechanisms, the search for radiation resistant materials, and industrial applications to the production or modification of materials of commercial interest. We shall be concerned mainly with the first aspect, which can be considered as an extension of the radiation chemistry of simple organic liquids and gases.

A book by Bovey (173) deals with the modifications produced in irradiation polymers but not with their production. A book by Charlesby (174) deals with polymerisation and grafting, but is largely confined to synthetic polymers. Much of the Mohler book (5) deals with the same subject. Two sections of volume three of the Haissinsky series (6a) deal with polymerisation and polymer modification. Shorter reviews have been given by Charlesby (175) and by Metz (176); and a series of articles of a more practical character has been published by Harrington (177).

### Polyethylene

*G values for crosslinking.*—Because of its apparent chemical simplicity and potential commercial interest, irradiated polyethylene continues to attract scientific attention. Yet, agreement has not been reached on such fundamental matters as the mechanism of crosslinking and degradation, and even the $G(X)$ values for crosslinking obtained by various methods and for different samples show wide divergencies. Busse & Bowers (178) summarised the present position, pointing out that reported $G(H_2)$ values vary from 3.0 to 5.7, $G(X)$ values range from 1.5 to 7.5 and $G$ (*trans*-vinylene unsaturation) from 1.2 to 2.2. The widest discrepancy arises for the $G$ values for

crosslinking $G(X)$. Recent values include: 1.60 to 1.66 from elastic measurements on both low and high density polyethylenes subjected to electron radiation [Charlesby, von Arnim & Callaghan (179)], 2.4 deduced from both elastic and swelling measurements [Waddington (180)], and the very low value of $G(X)=0.5$ for a range of 16 branched polyethylenes, [Busse and Bowers (178)]. For a *n*-paraffin, hexadecane, Dewhurst (119) obtained 1.8. The low value of Busse & Bowers was obtained from measurements of the gelation dose $r_{gel}$ and molecular weight $M_W$. For random crosslinking it can be shown theoretically that $r_{gel}M_W=0.48\times10^6/G(X)$. For the branched polyethylenes studied by Busse & Bowers $r_{gel}M_W\sim806{,}000$, the approximate constancy of this product serves to confirm the theory. However, the corresponding value of $G(X)$ of 0.6 is unusually low.

*Linear and branched polyethylene.*—Most of the earlier work on irradiated polyethylene was carried out with low density polyethylene, in which the average size and proportion of crystalline material is reduced by the presence of branches. The first measurements on linear polyethylene reported a different $G(X)$ value from the branched material. Measurements under similar conditions involving elastic modulus, unsaturation, swelling, and hydrogen evolution for different types of polyethylene show no significant difference in crosslinking [Epstein (181), Waddington (180), Charlesby, von Arnim & Callaghan (179), and Schumacher (182)]. It would appear therefore that crosslinking occurs as readily in crystalline as in amorphous regions, a conclusion difficult to reconcile with any theory of mobile radicals or chains. It is significant that paramagnetic resonance measurements indicate no significant concentration of radicals in linear polyethylene, unless oxygen is present [Abraham & Whiffen (183)]. Radicals observed in branched polyethylene may be associated with decomposition of branches.

Considerable differences are found [Waddington (180), and Charlesby, von Arnim & Callaghan (179)] when gelation dose and solubility above gelation dose are considered. The dose for incipient gelation increases in the order: Alkathene G2, Alkathene HD, Marlex 50, and Hostalen HD. If the product $r_{gel}M_W$ is constant, as would be expected if $G(X)$ is independent of the type of polyethylene, these results indicate that $M_W$ decreases in the same order for these polymers. This is feasible since a linear polyethylene could have a higher viscosity and a lower $M_W$ than a branched polyethylene.

*Crystallinity.*—Although it has often been said that exposure to radiation increases the melting point of polyethylene this statement is not true if it refers to the individual crystallites. In fact, radiation decreases their melting point by reducing their size. However, this effect is masked by formation of a crosslinked network which is amorphous above the melting point of the crystallites. Determinations of radiation-induced changes in the degree of crystallinity and crystallite size have been reported by Charlesby & Callaghan (184) who found that for equal energy absorption, pile radiation was far more effective in destroying crystallinity than electron or $\gamma$-radiation. This is ascribed to the high local density of ionisation and excitation in the

neighbourhood of a neutron collision. By comparing the reduction in crystallinity of irradiated samples at various temperatures with the melting point of normal paraffins, they were able to represent the crystalline distribution in both high and low density polyethylenes by an equivalent crystalline distribution of *n*-paraffins. The effect of radiation can then be seen clearly as a preferential destruction of the larger crystallites.

Irradiation causes slight changes in unit cell dimensions in polyethylene subjected to rather large doses of pile radiation, equivalent to about 250 megarads or more. Oriented fibres are quite sensitive to radiation damage of this character [Slichter & Mandell (185)]. These authors also followed the increasing constraint to molecular motion imposed by these crosslinks. Very large doses (several hundred megarads), are required to produce significant changes. The molecular motions in irradiated branched polyethylene were also studied using proton magnetic resonance, crystallinity, and dynamic properties [Fuschillo & Sauer (186)].

At low temperatures, crystallite destruction can take place after irradiation; Dole & co-workers (187, 188, 189) found that on heating and cooling irradiated polyethylene the crystallinity is further decreased, possibly by removal of internal stresses. This increased destruction of crystallinity occurs during irradiation, when this is carried out at 140°C. The effect of subsequent heat treatment on the crystallinity is also observed in dynamic modulus measurements [Woodward *et al.* (190)].

Irradiation with low energy ions causes considerable branching, a reduction in crystallinity, and a change in the *a* dimension of the orthorhombic cell [Sella & Trillat (191)].

*Oxygen effect.*—The role of oxygen has been further studied by Shinohara, Amemiya & Danno (192), by Schumacher (182), and by St. Pierre & Dewhurst (193). The former compared carbonyl and *trans*-vinylene unsaturation, produced by deuteron radiation and by x-rays, and found that the ratio of optical densities varied from about 0.7 to 15 according to the type of radiation. They deduce that the rate of oxygen diffusion cannot account for this difference, which they ascribe to the very different ionisation densities along the track of a deuteron and a Compton electron. This explanation should give a marked dependence of $G(C=C)$ on the type of radiation, even when treatment is carried out in vacuum, but no such dependence has been reported.

St. Pierre & Dewhurst (193) have reported on the role of oxygen which interferes with the crosslinking process. According to an earlier paper by Alexander & Toms (194), oxygen causes main chain fracture but does not interfere with the crosslinking reaction. In the experiments of St. Pierre & Dewhurst, oxygen at a higher pressure was used with a further apparent reduction in crosslinking, showing that the previous measurements did not represent limiting conditions. In earlier experiments by Dewhurst (117) oxygen was found to inhibit the dimerisation of hexane , carbonyl products being formed instead. They conclude therefore that oxygen does in fact in-

hibit the formation of crosslinks in polyethylene by combining with radicals, and forming unstable peroxide bridges which decompose under the extraction conditions used for gel determination.

Considerable differences in the aging behaviour of low density and high density polyethylene, exposed to oxygen after irradiation, were observed by Schumacher (182). The formation of carbonyl is ascribed in part to a reaction with unsaturated bonds rather than with trapped radicals, and there is a corresponding decrease in concentration.

*Unsaturation.*—A number of determinations of the $G$ value for *trans*-unsaturation have appeared recently. Using x-rays, Schumacher (182) obtained a $G$ value of 1.25 except at high doses when $G$ decreased. Busse & Bowers (178) obtained a similar value for a range of branched polyethylenes subjected to electron irradiation. Black (195) found a $G$ value for unsaturation in *n*-paraffins which decreased with molecular weight to about 3.3 for $C_{36}H_{74}$ and about 3.4 for polyethylene. Charlesby & Davison (196) obtained a value of 1.4 which varied little with temperature. Dole, Milner & Williams (188) derived values of 1.5, 1.8, and 2.2 for different types of polyethylene. They also investigated the reaction rates for vinyl and vinylidene groups initially present. The formation of unsaturation in polyethylene exposed to deuterons was studied by Shinohara, Amemiya & Danno (192) who found the same type of dose dependence of $G(C=C)$, as was observed with electrons and x-rays, decreasing at high doses; no absolute values are quoted. There is agreement that formation of *trans*-vinylene reaches a limiting value with increasing dose, presumably due to reaction with hydrogen produced elsewhere in the reaction. This is also demonstrated by the observation of Schumacher (192) that, when hydrogen is initially present at a pressure of 1 atmosphere, the $G$ value for this unsaturation is reduced by 30 per cent. The variation in the limiting value for $G(C=C)$ would therefore depend on the availability of hydrogen and could be modified by changing the radiation conditions. Dole, Milner & Williams (188) do report, in fact, different limiting concentrations of unsaturation depending on the degree of crystallinity.

It is estimated that half the hydrogen evolved results from C=C formation which occurs largely as a molecular process and has a zero temperature coefficient. The formation of unsaturation has also been studied in a number of low molecular weight hydrocarbons. Snow & Moyer (197), for example, found that unsaturation was connected with crosslinking, occurring more frequently in the dimerised paraffin molecules.

The destruction of vinyl and vinylidene unsaturation, originally present in polyethylene, has been studied in considerable detail by Dole, Milner & Williams (188), who confront several theories of crosslinking involving unsaturation with their data.

*Gas evolution.*—The gases evolved from irradiated polyethylene consist mainly of hydrogen, with small amounts of simple hydrocarbons, depending on the type of polyethylene studied. Dole, Milner & Williams (188) report $G(H_2)$ of 4.0, while Charlesby & Davison (196) obtained 3.1 for low density

polyethylene. The $G(H_2)$ for *n*-paraffin between $C_5$ and $C_{16}$ was reported by Dewhurst (117) to vary irregularly from 4.2 to 5.4, but he only obtained $G(H_2) = 3.1$ below the melting point. Schumacher (182) reports $G$ values for hydrogen evolution for both low and high density polyethylenes of between 2.2 and 3.1, increasing very slightly with temperature but being independent of dose up to 180 megarads. The other gases produced were mainly ethane, propane, and butane and amounted to only six per cent for low density (branched) polyethylene and one per cent in high density (linear) polyethylenes. Schumacher relates this difference to the number of end groups ($CH_3^-$) and deduces that main chain fracture takes place only near the ends of polyethylene molecules (and presumably at branched points which are particularly sensitive).

*Polypropylene.*—From the point of view of behaviour under radiation, polypropylene may be considered as lying between linear or branched polyethylene (which crosslink) and polyisobutylene (which degrades by main chain fracture). Several of the reactions occurring in irradiated polyethylene, such as degradation and hydrocarbon evolution, depend on the presence of branches; polypropylene can therefore be considered as an extreme case of branched polyethylene.

Solubility data on irradiated polypropylene [Black & Lyons (198)] show that both crosslinking and degradation occur, the former predominating by a relatively small amount. Considerable doses are therefore needed to reach the gel point and, due to the presence of numerous free ends, the crosslinked material has poor tensile properties. The gel point for polypropylene is reached for doses of 80 megarads [Black & Lyons (198)], and 12 to 50 [Waddington (180)], leading to net $G$ values for crosslink formation of between 0.6 and 1.3. From solubility measurements, Black & Lyons deduced that 1.2 crosslinked units and 0.9 main chain fractures occur per hundred ev absorbed. Formation of *trans*-unsaturation occurs at about the same rate as in polyethylene.

## Theories of Crosslinking

Calculations on network formation in polymers, carried out by Saito (199) take into account the possibility of cyclisation. This was ignored in previous work by Flory, Stockmayer and Charlesby. Inokuti and Watanabe (200) made quantum mechanical calculation of the reaction

$$—CH_2—CH_2— + H \rightarrow —CH_2—\dot{C}H— + H_2$$

and deduced activation energies for hydrogen attack on a paraffin chain. Later it was learned that the reaction of H with the end methyl group requires a lower energy than an attack on the middle of the chain.

One of the main difficulties in explaining crosslinking in solid polyethylene in terms of the combination of two independantly produced radicals, is to account for their mobility through the system. Accordingly, there is a strong tendency for theories to move away from the explanation of crosslinking in

terms of two mobile free radicals meeting at random, towards the view that a single ionisation or excitation gives rise to a crosslink.

Weiss (201) has reiterated the view that ionic reactions may account for crosslinking on the grounds that ionisation can be readily transferred throughout a molecule until it reaches a point at which neighbouring carbon atoms are sufficiently close to form a crosslink. A similar reaction is considered to account for double bond formation. Although there is now strong evidence for ionic reactions between molecules in the gas phase the efficiency of the process falls off with increasing molecular weight, and there is no direct evidence of the type of reaction proposed. If an ionic explanation for crosslinking is accepted, the presence of some radicals in low density polyethylene must be ascribed to other reactions (such as decomposition at branch points) not related to the main process of crosslinking.

Several theories of crosslinking [Pearson (202) and Simha & Wall (203)] assume mechanisms involving unsaturation; these have been criticised by Dole, Milner & Williams (188) for various reasons, including their assumption of a homogeneous system, which is certainly not valid for solid polyethylene.

The concept of endlinking, put forward by Charlesby, and involving *tri*-functional as against *tetra*-functional linkages has been extended by Dole *et al.* (188) to reactions involving unsaturated bonds. Thus

$$-CH{=}CH_2 \rightarrow -\dot{C}H-\dot{C}H_2$$

followed by

$$-\dot{C}H-\dot{C}H_2 + \begin{matrix}|\\ CH_2\\ |\end{matrix} \rightarrow -CH_2-CH_2-\begin{matrix}|\\ CH\\ |\end{matrix};$$

this process occurring simultaneously with crosslinking.

## Crosslinking Of Other Polymers

In reports on irradiated polyvinylchloride, there is doubt as to whether crosslinking or degradation is the main feature. Wippler (204, 205) has shown that crosslinking occurs in the absence of oxygen, and degradation in its presence, but even in the former case high doses are needed to reach the gel point, accordingly $G(X)$ is low. If, however, the polymer is irradiated in certain solvents, such as *tetra*-hydrofuran, crosslinking and gel formation take place more readily and at lower doses. Measurements of sol fraction and of molecular weight were compared with theoretical relationships, and used to derive information on the initial molecular weight distribution.

Studies of irradiated polyvinyl alcohol have been largely concerned with its behaviour in solution. Danno (206) has given some results on polyvinyl alcohol, either as a thin film or as a powder, irradiated with either $\gamma$-rays or fast deuterons. Results indicate that degradation occurs in the manner predicted by the theory of random main chain fracture, the energy per bond break being 56 ev. Most of the gas evolved consists of hydrogen. These

irradiations were carried out in air. Carbonyls (ketonic and acidic) were formed at a rate three times greater than main chain fracture. These polyvinyl alcohol samples contained adsorbed water; accordingly, it would be interesting to obtain data for dry polyvinyl alcohol in the absence of oxygen. In a later paper, Danno (207) describes the changes produced in irradiated polyvinyl alcohol by heat. Changes in weight occur and network structures are formed, the characteristics of which can be derived from swelling behaviour in boiling water. The weight changes are due to the loss of oxygen and hydrogen. A modified theory of endlinking is proposed to account for the observed gel formation.

The $\gamma$-irradiation of polyethylene oxide in vacuum was shown by Pearson (208) to lead to gel formation. Crosslinking was evidenced by an increase in viscosity up to the gel point at 50 megarads. When irradiation is carried out in air, however, the intrinsic viscosity falls. The network structure formed is readily attacked by exposure to oxygen; this is ascribed to the ease of attack at the tertiary carbon atoms. Results offer some evidence of a crosslinking rate which is not proportional to dose and this is explained in terms of a crosslinking mechanism proceeding via radiation-induced unsaturation.

Polycaprolactam contains some monomer and low polymer. Majury & Pinner (209) confirmed that the monomer was unaffected by electron or $\gamma$-radiation, due to the absence of any chain reaction. Chemical changes observed were crosslinking with a low $G$ value (0.35), and the fracture of amide bonds; these results are of interest in connection with the irradiation of proteins.

The effect of radiation on the mechanical properties of 66 nylon is described by Deeley, Woodward & Sauer (210) who measured the elastic modulus and loss at audio frequencies. These show a fall in modulus with temperature until the melting point is reached; above this point the modulus rises slowly. This behaviour is similar to that shown by polyethylene and indicates crosslinking. Evidence is also provided for the destruction of crystallinity. However, the degree of crosslinking deduced from the modulus is not proportional to the dose and saturates at 10 per cent. This is claimed to indicate a concurrent scission (degradation) of the main chain. Against this interpretation it may be argued that the properties of partly crystalline materials are particularly difficult to interpret when irradiation is carried out by mixed radiation from an atomic pile and furthermore the density of crosslinks, if high, cannot be deduced from the modulus by assuming rubberlike elasticity.

Some theories of crosslinking and degradation relate the distinction between these two reactions to heats of polymerisation and to polymer decomposition products. Polymers with low heats of polymerisation tend to decompose into monomer on pyrolysis, and degrade under radiation. Polymers with high heats of polymerisation produce little or no monomer, and crosslink. These theories have been tested by Burlant & Taylor (211) in the case of polyacrylonitrile and poly-$\alpha$-methacrylonitrile. In nitrogen the

former crosslinks while the latter degrades. In accordance with theory the former gives no monomer when pyrolysed and has a high heat of polymerisation (17.3 kcal./mole); the latter gives 85 per cent monomer on pyrolysis and its heat on polymerisation is estimated at 11 to 13 kcal./mole.

The radiation protective effect of the benzene ring (as in polystyrene) has been further demonstrated in crosslinking copolymers of styrene with butadiene [Bauman & Glantz (212)]. The situation with acrylonitrile copolymerised with butadiene is more complex. Copolymers of butadiene-styrene were also investigated by Turner (213) who was also concerned with the effect of additives on the crosslinking of rubber. He showed that these additives, considered to be acting as radical acceptors, can inhibit two-thirds of the radiation induced crosslinking; the remaining third is perhaps due to clusters of excitation or ionisation events. The possibility of energy transfer must also be considered. Certain halogenated compounds with a high $G$ value for radical formation, e.g., $C_2Cl_6$, can increase crosslinking.

## Reinforcement

Irradiation of rubber continues to attract attention because of possible improvements in the product as compared with conventional vulcanising techniques. Two tires of natural rubber and butadiene-styrene copolymer, containing no curing agents, chemical accelerators, or antioxidants, have been crosslinked by exposing them to radiation from spent fuel rods from an atomic reactor. Among the advantages claimed for this treatment are improved abrasion resistance, aging resistance, and uniformity of vulcanisation. Road tests on these tires are being carried out [Stockman, Harmon & Neff (214)].

The dose needed for optimum tensile properties of irradiated rubber is high (40 to 50 megarads), but improved mechanical properties can be obtained by incorporating carbon black to act as a reinforcing agent. Details of the mechanical properties of natural rubber, filled with various types of carbon black and subjected to various doses of radiation, are given by Charlesby, Burrows & Bain (215). For such filled rubbers the theoretical relationship between stress and strain does not apply. For all types of carbon black loading, maximum tensile strength occurs at a radiation dose of about 45 megarads. Although the elastic modulus for radiation and sulphur cures are similar the tensile strength of the radiation cured material is always lower.

The effect of fillers on various elastomers was also studied by Kuzminskii, Nikitina & Karpov (216). Among the additives tested were ZnO, chalk and kaolin (which increase the vulcanising rate as deduced from mechanical properties), and sulphur (which reduces this rate). The behaviour of these and other additives in radiation cure is different from that observed in conventional vulcanising.

The use of fillers to produce improved mechanical properties in irradiated elastomers was also studied by Duffey (217). The material studied was polyvinyl methyl ether which cannot be crosslinked chemically, and which has

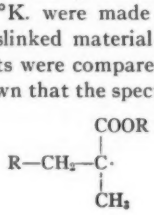
little tear resistance or tensile strength when crosslinked by radiation. These properties can be greatly improved by incorporating fillers such as silica, magnesia, carbon black, calcium phosphate, and iron oxide. For carbon-black filled polymers the maximum strength was reached at a radiation dose of about 50 megarads (as in carbon filled rubber), whereas with silica filled polymer, maximum tensile strength is reached at a lower dose. Magnesia proves to be a better filler than might be expected from its large particle size and its behaviour in other elastomers.

### Polymer Degradation

Glegg & Kertesz (218) continued their studies of irradiated cellulose, whose degradation may be related to the softening of fruit and vegetables exposed to $\gamma$-radiation. The decrease in intrinsic viscosity of solutions of irradiated cellulose made either from cotton cellulose or wood cellulose, was similar, whether the cellulose content was four per cent or 0.3 per cent. In the latter case, however, there was an after-effect, the viscosity decreasing over a period of several weeks. This after-effect is presumably due to trapped radicals, the presence of which was shown by paramagnetic resonance measurements.

Although poly-tetrafluoroethylene (Teflon) is known to degrade rapidly under irradiation its chemical inertness makes it difficult to deduce quantitatively the changes produced, such as the $G$ (chain fracture). In two Japanese papers the radiation damage caused is related to the physical changes produced. Nishioka, Tajima & Owaki (219) used the zero strength tensile ($ZST$) above the melting point as a measure of chain fracture and, for the range $10^2$ to $10^7 r$, found $\log ZST \propto \log r$. There was also an initial decrease in density followed by an increase above $10^4 r$. They concluded, somewhat surprisingly, that at these higher doses crystallinity is increased as a result of irradiation. Matsumae, Watanabe, Nishioka & Ichimiya (220) observed a drop in the melt viscosity $\eta$ following irradiation, and $\log \eta = A(1 - Br^n)$ where $A$, $B$, and $n$ depend on temperature. The transition temperature (327°C.) is unchanged, however, over the range $10^2$ to $10^7 r$; hence, one would not expect any marked changes in crystallinity.

The use of paramagnetic resonance to measure free radical concentrations in irradiated polymers has been described in several papers. Irradiated polymethylethacrylate gives a well-defined spectrum but there are considerable divergencies in the earlier interpretations given by Schneider, Uebersfeld, and Gordy. In the experiments by Abraham *et al.* (221) irradiations at room temperature and at 90°K. were made on polymethylmethacrylate, related esters and acids, crosslinked material (polyglycol dimethacrylate), and mixed esters. These results were compared with previous theories, and the conclusion tentatively drawn that the spectrum is due to the radical



coupling being with either four or three hydrogen atoms on adjacent C atoms, depending on the orientation. One difficulty is to explain the presence of only one type of radical resulting from main chain fracture. Moreover the corresponding $G$ value is 2.5, whereas the $G$ value for main chain fracture of poly-methylmethacrylate at room temperature is known to be 1.6.

Abraham & Whiffen (222) also give $G$ values for a range of polymers irradiated in vacuum. These are comparable in magnitude to those for crosslinking and degradation. A surprising feature is that high density (low pressure) polyethylene, with little chain branching or $CH_3$ content, gave no radicals. If radicals are trapped in irradiated polyethylene one would expect the residual radical density to be higher for the more crystalline polyethylene (which crosslinks as readily as the low density and less crystalline material), whereas, only the latter shows residual radicals when irradiated in vacuum. Another feature in the spectrum of certain polymers such as polytetrafluoroethylene is that radicals are only observed when oxygen is admitted to the system during, or after radiation.

## POLYMERS IN SOLUTION

Attention is now being paid to the irradiation of polymers in solution where changes produced can arise from two different causes, i.e., the direct effect of radiation on a polymer (direct effect) and the changes produced by the radicals formed in the irradiated solvent (indirect effect) which, if present, will be most pronounced at low polymer concentrations.

Reported work appears to fall into two distinct categories, those where the indirect effect predominates, as in aqueous solutions of certain polymers, and those where only the direct effect is observed, as in irradiation of polystyrene in organic solvents. These changes may be further modified by the presence of oxygen and by radiation protective effects.

In the irradiation of aqueous solutions of polyvinyl alcohol and polyvinyl pyrollidone (224), the dose for gel formation decreases with lowered concentration, as is to be expected if crosslinking occurs both by the direct effect and by the indirect effect. However, the minimum gelation dose is reached at about one per cent polymer concentration, below which the dose rises rapidly and no gel can be formed at concentrations less than 0.3 per cent.

The result of investigations designed to explain the cause of this relatively sharp transition have been published by Berkowitch, Charlesby & Desreux (225) and by Danno (226). The former deals specifically with the transition region below three per cent. Below the concentration at which gel can be formed the intrinsic viscosity still rises to a maximum as does the weight average $M_w$. The explanation of the phenomenon is that crosslinking occurs at all concentrations, but at the lowest concentrations most of these crosslinks are formed within the polymer molecule which therefore shrinks. Only a small proportion of the links are with other molecules, and these give rise to

a micro-gel. The critical concentration for formation of a macro-gel would therefore depend on the configuration of the molecules in the solution and on the degree of overlap between adjacent molecules.

Danno (226) has also investigated the molecular weight of polyvinyl alcohol as a function of dose and initial molecular weight. Above a critical concentration of 0.36 per cent (depending on initial molecular weight), the degree of polymerisation increases with dose to infinity whereas below it there is a decrease with a subsidiary peak. The energy per crosslink is 62 ev, a result in reasonable agreement with the $G$ values of crosslinking or other polymers. The same explanation of internal crosslinking is advanced to account for these effects and from the critical concentration a segment length of six monomer units is deduced. The rather complex nature of the mol. wt./dose curve at low concentration is tentatively ascribed to a combination of crosslinking and degradation, but if these molecular weights are based on intrinsic viscosity data this interpretation is not necessarily valid owing to the formation of branched molecules.

Papers by Durup (227, 228) and by Henglein & Schneider (229, 230) deal with radiation effects in polystyrene dissolved in organic solvents. Crosslinking takes place in the solid and in the more concentrated solutions. The kinetics indicate two distinct processes, one a result of a short-lived intermediate, the other a result of a relatively stable structure. Protection against degradation is afforded, e.g., by ethanol. According to Henglein & Schneider, both crosslinking and degradation take place, the ratio depending on the solution. For example, in $CCl_4$ there is only degradation, whereas, in poor solvents such as ethyl acetate, polystrene forms micro-gels, and crosslinking occurs. These processes take place by a free radical mechanism as can be shown by the inhibition of crosslinking by suitable additives.

Baxendale & Thomas (231) studied the degradation of polymethacrylic acid in aqueous solutions exposed to either ultraviolet or x-rays. In the absence of air the $G$ value for main fracture by x-rays is 1.05 as compared with 1.6 for the dry polymer. In the presence of air, this $G$ value decreases to 0.64, but is increased to 1.68 in the presence of $H_2O_2$. The authors conclude that degradation is due to the hydroxyl radicals produced by radiation, a conclusion differing from that previously reached by Alexander *et al.* In the x-ray degradation of polymethacrylic acid the following $G$ values are obtained $G(H_2) = 0.58$, $G(CO_2) = 0.25$, and $G$(isobutene) $= 0.15$.

Apart from such well-explored changes as dimerisation, degradation, and changes in unsaturation, changes in isomerisation have been observed in polymers. The results obtained by Golub (223) for polybutadiene may be compared with those previously found in irradiated olefins, and may be assumed to involve excitation of the $\pi$-electrons to a higher energy level, sufficient to overcome the barrier to free rotation. The reaction is greatly increased by the addition of sensitizers such as ethyl bromide, when it parallels photochemical changes. Such sensitised solutions may be of value as high intensity dosimeters.

## POLYMERISATION

Previous work in radiation induced polymerisation has frequently been directed towards the study of reaction kinetics, when the rate of formation of initiating radicals is directly proportional to the radiation intensity $I$. At low intensities, at which termination occurs by the combination or disproportionation of two growing chains, the rate of the reaction varies as $I^{0.5}$. In certain systems, however, departures from this relationship are observed; some polymerisation continues after cessation of irradiation, probably due to trapped radicals. At the Prague Symposium, Bensasson & Bernas (232) reported on this after-effect in acrylonitrile, which is observed when the polymer is produced in a precipitating medium. The investigation covers the velocity and activation energies of the post-polymerisation reaction which seems to give branched polymer. Chapiro & Sebban-Danon (233) studied the polymerisation of styrene, methylmethacrylate, and acrylonitrile at higher radiation intensities than those at which the usual $I^{0.5}$ dependence is found. For acrylonitrile, in which there is an after-effect, the initial dependence is as $I^{0.8}$. At higher intensities, drop in yield is caused by the combination of two primary radicals. Burlant & Adicoff (234) deal with the influence of physical state on the polymerisation kinetics of vinyl stearate and report a discontinuity in both the polymerisation rate and the average molecular weight at the melting point of the monomer. This is ascribed to a change in the diffusion rate constant for propagation. The polymerisation rate varies directly as the radiation intensity. This is taken to indicate that polymerisation occurs in individual volume elements.

At the Paris Conference on Radioisotopes, Medvedev (235) gave a brief survey of Russian work on polymerisation, mainly with the polymerisation of ethylene under various conditions in solutions. This can lead either to a higher yield, or to formation of low molecular weight polymers (telomers) such as $Cl(C_2H_4)_nCCl_3$.

d'Emaus *et al.* (236) carried out preliminary work on the synthesis of butadiene-styrene copolymers. The $G$ value for these chain reactions is relatively low; a typical dose of 20 to 30 megarads gives about 10 to 20 per cent of conversion. Lower doses suffice when the material is irradiated as an emulsion. A more promising line consists in irradiating mixtures of unsaturated hydrocarbons with $SO_2$. These reactions, which can be initiated chemically or by light, give polymers with $G$ values in the $10^4$ range. The most interesting copolymer is obtained from propylene and $SO_2$, the yield being 90 per cent at 0.7 megareps; the softening range of the copolymer is about 280°C.

Although radiation produces both ionised and excited species directly, most polymerisation reactions initiated by radiation have been found to proceed by free radical mechanisms, similar to those initiated by chemical initiation or ultraviolet light. Evidence has now appeared for a specific ionic reaction in isobutylene, irradiated at low temperatures [Davison, Pinner & Worrall (237)]. Two of the distinctive features of the reaction are its tempera-

ture variation (increasing yield with decreasing temperature) and lack of dependence of yield on the radiation intensity. The possibility of initiating ionic reactions with high energy radiation opens up a new field of research which is absent in photo-chemistry. Burlant & Green (238) have attempted to extend this to other polymers and have studied mixtures of various monomers (styrene, methylmethacrylate, 2-vinyl pyridine, vinylidene chloride, etc.), but these mixtures show the same reactivity rates as for radical polymerisation. However, some evidence is claimed for an ionic contribution in the polymerisation of isoprene. A further feature is the lack of temperature dependence of the reaction.

In most cases, irradiation of catalysts has produced relatively small changes in their activity, but when materials such as ZnO, silica powder, and MgO are added to isobutene, tenfold increases in yield can be obtained in the ionic reaction [Charlesby and Worrall (239)]. This reaction points to an increased surface reactivity of these materials, capable of increasing the initiation rate.

### Graft and Block Copolymers

Radiation offers a very effective method of producing graft polymers. Two main methods are available, the irradiation of the polymer backbone in the presence of the monomer, and the irradiation of polymer in the presence of oxygen to form peroxide groups which can subsequently be decomposed thermally in the presence of monomer to give grafts. The rate of the grafting reaction depends on a number of factors including radiation dose and intensity, monomer absorption and diffusion rate, and temperature, as well as on the reactivity ratios and termination mechanism. These various factors determine the character of the graft, such as the chain length, number of branches, and the undesirable formation of homopolymer. Much work remains to be done to relate these characteristics, on the one hand to the physical properties of the final product, and on the other, to the conditions of formation.

Charlesby & Pinner (240) studied the effect of radiation intensity, of equilibrium absorption, and of diffusion rate on grafting to polyethylene. For styrene grafts the rate of grafting is approximately linear, even at high radiation intensities, due to the low reactivity of the monomer and to its high absorption in polyethylene. For other monomers, such as methylmethacrylate, the monomer initially present is rapidly used up, and the rate of diffusion of further monomer into the system is insufficient to cater for the reaction, so most of the grafting occurs on the surface. This preferential grafting may be avoided by reducing the radiation intensity or by intermittent irradiation and soaking in monomer. As a result of the Trommsdorf effect reducing polymer diffusion, the rate of grafting at very high radiation intensities is greater than would be expected for polymerisation of the pure monomer; this renders more feasible the practical use of electrical sources of radiation for producing graft polymers.

The effect of radiation intensity on the rate of grafting of styrene on to polyisobutylene has been studied by Sebban-Danon (241). At low degrees of conversion and at low intensities the reaction varies as $I^{0.5}$ but increases to about $I^{0.75}$ at high conversions because of the Trommsdorf effect. Two possible termination mechanisms are involved, one bimolecular, the other monomolecular, due to the formation of trapped radicals.

Henglein, Schnabel & Heine (242) investigated several graft systems from the point of view of diffusion control which can give rise to either surface or to volume grafts. In the former case, solvents for the original polymer can swell or extract the inner part of the specimen. A wide range of such copolymers is possible, and a study of such systems should provide interesting information on osmotic effects.

The peroxide method of producing graft copolymers on polyethylene has been investigated in detail by Chapiro (243), for both methylmethacrylate and acrylonitrile. Among the variables studied were time and temperature of heating the oxidised film in the presence of monomer. Different activation energies were observed below and above the melting point of the crystallites, and the method may be of interest, not only from the point of view of grafting, but also as a method of studying diffusion rates, and the stability of crystals.

Attempts to measure the number of active centres responsible for grafting in the peroxide technique were made by Burlant & Green (244). Diphenylpicryl hydrazyl was used as a radical scavenger; and for linear polyethylene radicals were found only for radiations carried out in air, a result in conformity with paramagnetic resonance measurements. For polymethylmethacrylate, however, stable radicals were also formed when radiation was carried out in nitrogen. The molecular weight of the homopolymer formed during grafting was taken as a rough measure of branch chain length and lay in the range $10^5$ to $10^6$. High-intensity electron irradiation doses, of the order of 10 megarads, gave roughly $10^{-3}$ moles of OOH per mole of monomer in the polymer. This may serve as a measure of the branching density under these conditions. Burlant & Breen also reported that the ability to graft with peroxidised polyethylene decreases rapidly in a few weeks after radiation, a result which conflicts with the statements of Chapiro.

Turner and colleagues have been concerned with the formation of methylmethacrylate-rubber graft and block copolymers, produced either mechanially, chemically, or by irradiation. In radiation-induced grafts, little polymethylmethacrylate homopolymer is formed unless a transfer agent is present or radiation induced degradation occurs [Angier & Turner (245)]; chemical initiation may give more free homopolymer. The gamma-grafted methyl methacrylate chains are of high molecular weight ($>10^6$) [Turner (246)]. Comparison of the grafts of methyl methacrylate in rubber latex, initiated chemically or by radiation, show considerable difference in their properties, depending on the distribution of the methyl methacrylate throughout the lattice [Turner *et al.* (247)]. These differences are due to the

location of the initial radicals either on the surface or throughout the latex particles, the former giving an inferior product consisting of discrete particles rather than a continuous film. By the use of suitable chemical catalysts, capable of initiating radicals within the latex particles, this difficulty can be overcome.

Block copolymers of methyl methacrylate and polyvinyl acetate can be obtained if the latter is itself polymerised by gamma irradiation as an emulsion of the monomer. Initiation of grafting is then caused by trapped radicals in the polymer. However, the yield is considerably greater than may be expected from theory and in distinction from the work described above, large excesses of homopolymer are formed. This observation is explained by the absence of chain termination resulting from combination of two growing chains, which is due to the low initiating radical concentration. Methyl methacrylate chain growth is limited only by a chain transfer reaction. This also accounts for the formation of homopolymer. Similar conditions arise when grafting styrene in emulsion to previously irradiated polymethyl methacrylate film [Allen *et al.* (248)].

### Polyesters

Several early papers have described the use of radiation as a means of curing polyester resin mixtures, but the results obtained were largely descriptive. A few papers recently appeared which attempt a more quantitative analysis of the reaction. In a typical system an unsaturated polyester containing ethylenic unsaturation is mixed with a vinyl monomer, such as styrene, and the viscous liquid obtained is set to a dense three-dimensional network structure by the use of chemical catalysts and heat. Using chemical catalysts, it had proved difficult to relate the properties to this network to the density of crosslinks or to the number of double bonds reacted. With radiation the number of initiating radicals can be closely controlled and a much closer study of reactions may be made.

The practical advantages of the irradiation technique lie in the absence of catalyst fragments after the reaction, and the reduced heat rise due to the exotherm.

In a paper by Charlesby & Wycherley (249) many of the properties of commercial mixtures cured by radiation were compared with similar mixtures cured catalytically. The fully cured system showed very similar properties. By reducing the doses involved, it became possible to produce semicured materials which can be reshaped and fully cured by further irradiation or by conventional catalytic methods. It is significant that the rate of the reaction is considerably greater than would be expected from straightforward polymerisation at these very high radiation intensities.

A wide range of commercial polyesters, incorporating either styrene or diallyl phthalate, was investigated by Colichman & Scarborough (250). Only small improvements (20 per cent) in tensile strength and Young's modulus were obtained when thermally cured materials were subsequently

irradiated. With $\gamma$-radiation at 10 megarads/hr., the dose needed for full cure is 5 to 10 megarads, very close to the doses (about 6 megarads) used by Charlesby and Wycherley with electron radiation at much greater intensities. These low doses indicate that the process occurs by a chain reaction but, unlike vinyl polymerisation, the rate of the reaction is approximately proportional to the radiation intensity, so that chain termination is not due to the combination of two growing chains.

The mechanical properties of polyesters cured by radiation were investigated by Charlesby & Fukada (251). The maximum mechanical damping corresponds to the softening point of the network formed, and it was found that (above a certain dose) this temperature varies but little, and the Young's modulus approximates to that in a conventional catalytic cure.

For lower radiation doses a semicured material is obtained whose modulus after heating is greatly increased. This change must be ascribed to radicals trapped in the system which can only react further when sufficient flexibility is given to the molecular chain. The degree of cure of these polyesters is therefore not limited by the availability of initiating radicals. It would be desirable however to extend this work, irradiating at higher temperatures, to give greater mobility to the polyester chains.

In a cured polyester not all the unsaturated groups are converted; methods used to evaluate the number which have reacted involve either dilatometric measurements or studies of incipient gelation. Shultz (252) used a new technique whereby the fully cured network is exposed to radiation and the decomposition products studied. The proportion of soluble material produced can be evaluated in terms of the number of radiation-induced main chain fractures and of bridges present in the fully cured material. From the relation between solubility and radiation dose, Shultz deduced that rather more than 50 per cent of the doubly reacted ethyl dimethacrylate units were lost to small ring formation within each chain.

The theoretical derivation of the kinetics of network formation by a chain reaction has been given [Charlesby (253)]. This differs from conventional random crosslinking in that the gel point occurs at a very low crosslinking density and beyond this gel point the relationship between soluble fraction and radiation dose approximates to an exponential relation. Experimental investigations of reactions showing this character are described by Charlesby, Wycherley & Greenwood (254) who subjected some unsaturated polyesters (with no vinyl monomer) to radiation, and studied the change in viscosity or solubility. Both the change in viscosity, up to the gel point, and the decrease in solubility beyond this point were found to be substantially independent of radiation intensity, thereby indicating that these polymerisation chains do not terminate by combination or disproportionation of two independent chains. The low gelation dose, and the shape of the sol fraction/dose curve differed from those for conventional crosslinking and were in accordance with the theory of network formation by a chain reaction. The degree

of unsaturation and the molecular weight of the polyester had little effect and the reaction was less rapid at higher temperatures.

A comparison of the effect of additives on radiation and thermal catalytic cure show their inhibiting effects to be identical except in the case of anthracene where there was evidence of radiation protection by energy transfer.

These results indicate the considerable difference between this type of chain reaction, and conventional polymerisation or crosslinking.

## DOSIMETRY

Appreciable effort continues to be devoted to the development of chemical methods for measuring radiation doses. The greatest needs at present seem to be: firstly, for civil defense purposes, a simple and robust, but not necessarily highly accurate, dosimeter capable of measuring doses below 500 rads; secondly, for radiobiological and radiotherapeutic use, a more accurate dosimeter measuring doses below about 5000 rads; and, thirdly, for use with industrial irradiation units, a dosimeter measuring doses of $10^6$ rads and up. Minder, giving 120 references, recently reviewed radiation dosimetry by chemical methods (255). Feng has proposed the degradation of polystyrene dissolved in carbon tetrachloride as the basis for chemical dosimetry over the whole range from $10^2$ rads up to as high as $10^5$ rads (256).

Reigert and Spinks studied the energy dependence of silver phosphate glass dosimeters for 100 kev to 24 Mev. These robust dosimeters are useful in the range 100 to 1000 rads (257). Both Downes (258) and Armstrong & Grant (259) have proposed sensitive methods based on aqueous benzoate. Downes suggests measuring the $CO_2$ formed from $C_6H_5C^{14}OOH$, and Armstrong & Grant suggest using a spectrofluorimetric method to measure the salicylic acid formed. These methods can measure doses of 10 to 100 rads. For a slightly higher range, up to 100 rads, the coloration of aqueous solutions of 4,4′-(5-chloro-2-thenylidene)bis[N,N-dimethyl aniline] has advantages, and Armstrong & Grant have thoroughly investigated the factors influencing the system (260, 261).

In the range up to 50,000 rads, the ferrous sulphate system (Fricke dosimeter) is pre-eminent. Sinclair & Shalek (262) briefly report another calibration of the system for 200 kv. x-rays. Cobalt-60 $\gamma$-rays, and 22 Mev x-ray. They find no difference between the yields for the two more energetic radiations, $G$ in 0.8$N$ sulphuric acid being 15.6. Allen & his colleagues find that the yield in 0.1$N$ sulphuric acid is 2.8 per cent lower than in 0.8 $N$ sulphuric acid (63). Hoecker & Watkins suggest using the gelation of a polyester-styrene system as a measure of dose (263). This system appears to have few advantages over the Fricke dosimeter, and numerous disadvantages, such as dose-rate dependence, and inconvenience in preparation.

Methylene blue in aerated aqueous solution is still being proposed for use. Lafuente, Goldblith & Proctor have discussed some of the difficulties (264) but believe the system might be useful for doses up to nearly $10^7$ rads.

Minder however prefers to restrict its use to doses below $10^4$ rads (255). Ceric sulphate is a more promising system for the range $10^5$ to $10^6$ rads. Whittaker (265) reports a yield of $G=2.36\pm0.12$ cerous ions formed per 100 ev, a yield in good agreement with $2.45\pm0.8$ as found previously by Johnson and Weiss.

In the high dose region, Artandi & Stonehill recommend measuring the colour produced from rigid polyvinyl chloride films (266). One of the most promising ideas for quantitative use is to measure the colour produced in irradiated polymethyl methacrylate or polyethylene terephthalate (267), and further reports on this system, which appears useful up to $10^8$ rads, are awaited with interest. The incorporation of a dyestuff, Sudan III, into polyethylene has been patented as a method of dosimetry, the colour changing from red to orange on irradiation with doses in the region of $5–15\times10^6$ rads (268).

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# QUANTUM THEORY[1,2]

## THEORY OF MOLECULAR STRUCTURE AND VALENCE

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The first and major part of this article is a survey of recent quantum-mechanical work on those magnetic properties of simple molecules that are closely related to electronic structure. This is followed by a brief description of some of the papers on molecular wave functions that have been published during the past year.

### MAGNETIC PROPERTIES OF MOLECULES

During the past few years, a considerable amount of attention has been devoted to magnetic properties of molecules. Classical experimental work on magnetic susceptibilities is now supplemented by the electron and nuclear magnetic resonance techniques which give further information about the behaviour of molecules and free radicals in a magnetic field. The theoretical interpretation of these data has been studied by a number of workers in the field of molecular quantum mechanics and has led to some additional understanding of electronic structure. Here we shall review some of these developments, emphasizing work on molecules containing only atoms in the first row of the periodic table.

*Diamagnetism.*—The phenomenon of diamagnetism, shown by the great majority of molecular substances, arises from the electronic orbital currents or circulations induced by an external magnetic field. The general quantum-mechanical theory of the diamagnetic susceptibility was given many years ago by Van Vleck (1), but, as with many other branches of quantum chemistry, the detailed application to any but the smallest molecules has been hindered by the lack of knowledge of electronic wave functions and the difficulty of appropriate computing techniques.

The Van Vleck formula for the molar diamagnetic susceptibility $\chi_z$ in the z-direction takes the form

$$\chi_z = -\frac{Ne^2}{4mc^2}\sum_i (0|\, x_i^2 + y_i^2 \,|0) + \frac{Ne^2}{2m^2c^2}\sum_n{}' \frac{|\,(n|\, L_z \,|0)\,|^2}{E_n - E_0} \qquad 1.$$

where $(x_i, y_i, z_i)$ are the coordinates of the $i$th electron and $L_z$ is the z-component total electronic angular momentum operator. The summation, $\sum'$, is over all excited states. The molecular susceptibility is a tensor, and the mean value observed in measurements on a fluid phase is the average $\chi$ of the three principal components. The actual form of equation 1. depends on the choice of the vector potential of the external field, and the values of

[1] The survey of the literature was completed in October, 1958.

[2] The following abbreviation will be used: LCAO (linear combination of atomic orbital).

the two terms both depend on the choice of origin. The total value of $\chi$, however, must be independent of origin; and it can be shown in detail that a change of origin leads to equal and opposite changes in the two parts. The first term in the Van Vleck formula (equation 1.) represents the effect of a uniform rotation about the $z$-axis with the angular frequency $eH/2mc$ in a magnetic field $H$. For atoms in $S$-states and linear molecules in $\Sigma$-states with the external field parallel to the axis, this is the only term (since the electronic angular momentum $L_z$ is zero). The second term in the formula represents the correction to this picture and, because it always gives a positive contribution to $\chi$, it is often referred to as the temperature-independent paramagnetic term. Alternatively it can be considered as measuring the stabilization as a result of the mixing of ground and excited electronic states by the external field. Wick (2, 3, 4) pointed out that the value of the temperature-independent paramagnetic term (using the centre of mass as origin) could be obtained experimentally from a measurement of the magnetic moment of a molecule in a particular rotational state. A number of such determinations have been made (2, 3, 5, 6, 7).

Although equation 1. is a complete expression for the diamagnetic susceptibility, successful calculations based on it have been limited for two main reasons. The first of these is that for all except the smallest molecules, the two terms are of opposite sign and largely cancel, so that both have to be calculated accurately to get a reliable result. The second is that the calculation of the paramagnetic term requires a detailed knowledge of excited states which is not often available. This second difficulty can be partly overcome by replacing the excitation energies in the denominators by some average value which can then be taken outside the summation sign. The summation can then be carried out to give $(0|L_z^2|0)$, so that the problem is reduced to the calculation of the value of the mean-square angular momentum in the ground state. This is relatively straightforward if a good wavefunction is available. However, there is considerable uncertainty about the value to be used for the mean excitation energy in such a calculation. This point was discussed in detail by Weltner (8). Other authors have avoided altogether the difficulties inherent in the perturbation theory by using a variational function with suitable parameters.

The magnetic susceptibility of the hydrogen molecule has been investigated theoretically by a number of authors (8 to 13). This molecule is exceptional in that the high frequency or paramagnetic term is relatively unimportant if the origin is taken at the centre of the bond. The experimental value of the total molar susceptibility (14) is $-3.97\times10^{-6}$, the paramagnetic contribution (15) being only $+0.0846\times10^{-6}$. The diamagnetic term has been calculated directly using various ground-state wave functions. Wittmer carried out such a calculation for the accurate 11-term James-Coolidge function and obtained a contribution to the molar susceptibility of $-4.15\times10^{-6}$. Perturbation calculations of the high-frequency contribution based on the use of an average excitation energy $\Delta E$ have also been carried out, but these

turn out to be considerably greater than the experimental value unless a large value of $\Delta E$ is used (8). Variational calculations have been more successful, and those of Ishiguro & Koide (12) and Tillieu & Guy (13) have given results in substantial agreement with experiment. The latter authors use a variation function of the form $\psi = \psi_0 (1 + g \cdot H)$ where $\psi_0$ is the unperturbed wave function, $H$ is the applied magnetic field and $g$ is a variable vector function of electronic coordinates. Quite simple forms for $g$ of appropriate symmetry give satisfactory results. These authors have made a complete calculation of the susceptibility along and perpendicular to the molecular axis; and they have concluded that diamagnetism is least along the axis, in spite of the fact that there is no paramagnetic term in this direction.

Several calculations of magnetic susceptibility have also been carried out on the tetrahedral molecule $CH_4$. Early work assumed that because of the high symmetry the paramagnetic contribution is small (it is zero for spherical symmetry), so that the calculation reduces to the evaluation of the mean-square distance of the electrons from the central nucleus. Buckingham, Massey & Tibbs (16) using a Hartree-type self-consistent function based on a "smeared proton distribution" obtained a value of $-33.2 \times 10^{-6}$ for the molar susceptibility, which is much larger than the experimental value (17) of $-12.2 \times 10^{-6}$. The calculations of Coulson (18), using molecular orbital and electron pair wave functions, also gave large values of $-26.6 \times 10^{-6}$ and $-27.7 \times 10^{-6}$, respectively. Further calculations including ionic terms in the wave function have been made recently by Venkatachalam & Kabadi (19) giving $-21.1 \times 10^{-6}$, although it is rather difficult to reconcile this lower value with the bond polarity $C^+ - H^-$ assumed. Recently it has been suggested that the discrepancy between these calculated values and experiment arose because the paramagnetic contribution was much larger than had been supposed hitherto. No experimental value of this contribution from the rotational magnetic moment is available, but Weltner (8, 20) has pointed out that an approximate estimate may be made from the corresponding rotational moment of the methyl group in $CH_3 - C \equiv C - D$, which has been obtained from microwave measurements. He finds that this would correspond to a positive contribution of $+9.3 \times 10^{-6}$ to the susceptibility of methane and thus account for much of the difference. Carter (21) has also considered the value of this term and has pointed out that, if there was no interaction at all between the atoms of methane, the paramagnetic contribution is easily calculable in terms of the C—H bond distance and would lead to a contribution of $+12.6 \times 10^{-6}$. So it seems quite possible that the early assumption that the paramagnetic contribution was negligible was not justified. A variational calculation of the magnitude of this term would be of considerable interest but has not yet been undertaken.

The theory of the diamagnetic susceptibilities of aromatic hydrocarbons has been studied in a considerable number of papers. These compounds always show a marked magnetic anisotropy, the susceptibility being greatest when the applied field is perpendicular to the molecular plane. This is pri-

marily a result of the interatomic currents induced in the $\pi$-electron system. A semiclassical theory of the anisotropy based on an equivalent electrical network was developed by Pauling (22) and was followed shortly after by a quantum-mechanical treatment based on the simple Hückel-type LCAO molecular orbital method of London (23). The London theory gives a statisfactory account of the diamagnetic susceptibility of polycyclic hydrocarbons relative to benzene. More recently it has been extended to a wide number of compounds including $p$-polyphenyls and polyacenes by McWeeny (24, 25, 26), who also gives some empirical rules for making approximate estimates for large molecules. Another development of the London theory is the calculation of the distribution of current and induced magnetism within the molecules due to Pople (27).

Attempts at a nonempirical calculation of the diamagnetic anisotropy of benzene itself have given generally a value lower than the experimental result. A more refined molecular orbital calculation based on a complete antisymmetrized molecular orbital function for the $\pi$-electrons was carried out by Fujii & Shida (28), but gave only 74 per cent of the observed value. Itoh, Ohno & Yoshizumi (29) carried the theory a stage further by including configuration interaction, but this lowered the calculated value further. A number of suggestions have been made to account for this discrepancy. Lykos & Parr (30), for example, point out that the area of the benzene ring's appearance in the various formulae is really a quantum-mechanical average which can be calculated more accurately and is a function of the Slater constant $Z$ of the atomic $2p\pi$ orbitals. They show that if $Z$ were as small as two, most of the difference would be accounted for. Singh (31) has suggested that the anisotropy of individual C—C bonds may contribute to the over-all anisotropy of the molecule. Another possibility is that there are also ring currents associated with the $\sigma$-electron framework, but no theoretical calculations of these have been attempted.

*Nuclear magnetic shielding.*—The frequency which is observed in nuclear magnetic resonance experiments is a measure of the local magnetic field experienced by a nucleus when the molecule of which it forms a part is placed in an external magnetic field. Since the external field induces diamagnetic electronic currents which set up secondary fields, this local field will be modified by an amount depending on the chemical environment. If the external field is $H_0$, the local field can be written $H_0(1-\sigma)$ where $\sigma$ is a nondimensional constant measuring the electronic magnetic screening. Differences between values of $\sigma$ are referred to as "chemical shifts." The magnetic moment of the nucleus therefore is effectively used to explore this secondary magnetic field, and, in consequence, the theory of the screening constant $\sigma$ is closely related to that of the diamagnetic susceptibility.

The general theory of nuclear magnetic screening in molecules was first developed by Ramsey (32), who derived a formula essentially parallel to the Van Vleck susceptibility formula (equation 1.). Ramsey's result is again a sum of two parts, the first representing the effect of the secondary magnetic field of the Larmor circulation of the electrons about the nucleus and the

second the effect of the "paramagnetic" mixing of the ground and excited states of the molecule by the external field. Like the diamagnetic susceptibility, the screening constant is really a tensor since its value depends on the orientation of the external field relative to the molecular axes. The effect of rapid molecular tumbling in liquids is effectively to replace this tensor by its mean value $\sigma = \frac{1}{3}(\sigma_{xx}+\sigma_{yy}+\sigma_{zz})$.

As with diamagnetism, the theory is greatly simplified for free atoms in $S$ states where the paramagnetic term is zero. The diamagnetic term then is reduced to a calculation of the mean value of $r^{-1}$ where $r$ is the distance of an electron from the nucleus. This result was first obtained by Lamb (33) and has been used to estimate the nuclear screening for a large number of atoms by Dickinson (34) using Hartree type self-consistent wave functions where available and interpolating elsewhere.

Calculations of the screening constant of nuclei in molecules are much more difficult because of the paramagnetic term. Once again, a full treatment by perturbation theory requires a complete knowledge of excited states. The only system for which a precise calculation has been carried out is a hydrogen atom placed in an electric field which removes the spherical symmetry (35). A large number of calculations on the hydrogen molecule have been reported, using various available wave functions. In close analogy with the relation between the rotational magnetic moment and the paramagnetic term in the diamagnetic susceptibility expression, Ramsey (32) showed how the paramagnetic term for linear molecules is proportional to the nuclear spin-rotational interaction constant. This can be measured experimentally using molecular beams. Combining such a result for $H_2$ with a value of the first term calculated from simple wave-functions, Ramsey obtained the mean screening constant $\sigma$. His result was slightly modified by Newell (36) who obtained $\sigma = 32.1 \times 10^{-6}$ using the diamagnetic term only, and $\sigma = 26.6 \times 10^{-6}$ after correcting for the paramagnetic term. Direct calculations of the magnitude of the paramagnetic contribution to $\sigma$ have been carried out by a number of authors. Some of these are based on an approximate form of Ramsey's formula replacing the excitation energy by a mean value, and others have used variational methods. Das & Bersohn (37) and later Stephen (38) used the variational method originally suggested for the susceptibility by Tillieu & Guy (13) and obtained good agreement with the "experimental" value of Ramsey. A direct calculation of $\sigma$ using gauge-invariant atomic orbitals has been published by Hameka (39).

McGarvey (40) has also carried out variational calculations of the paramagnetic contribution to $\sigma$ for the hydrogen halides and has obtained results in reasonable agreement with the experimental trend in this series. Stephen (38) has attempted a similar calculation on the proton screening in various types of C—H bonds, but agreement with experimental data is less satisfactory. It seems likely, however, that variational methods will prove more useful in future accurate calculations of screening constants than will direct application of the Ramsey expression.

The difficulties associated with the application of the general method

have encouraged some rather more-empirical approaches to the theory of nuclear magnetic screening. These have been based on a division of the total screening into separate atomic contributions in a way originally suggested by Saika & Slichter (41). They divided the total screening into three parts: (*a*) the diamagnetic correction for the atom in question, (*b*) the paramagnetic correction for the atom in question, and (*c*) the contribution from other atoms. The physical significance of this separation lies in the division of the total induced current density into circulations within individual atoms. The mathematical basis of this breakdown and its relation to general theory has been discussed by Pople (42) and McConnell (43) who have also indicated how it can be extended to allow for the magnetic effects of more delocalized interatomic currents such as those flowing round closed paths in cyclic molecules. On the basis of this breakdown, Saika and Slichter developed a quantitative theory of the atomic contributions to the screening constant for fluorine nuclei. Experimental observations of fluorine chemical shifts show a fairly good correlation with the electronegativity of the atom to which the fluorine is bonded, a covalently-bonded $^{19}F$ nucleus being less screened than an ionic one. The magnitude of these shifts however, are too large to be explained by the effect of the increase of electron density on the atom in the ionic compounds and consequent increase in Lamb's diamagnetic term. Saika and Slichter showed that the shift could be explained by variation of the local paramagnetic contribution, this being greatest in the $F_2$ molecule and least in the purely ionic isolated $F^-$ ion. The magnitude of the paramagnetic contribution is dependent on the properties of the particular excited states which become mixed with the ground state by the magnetic field, so that accuracy of such calculations is limited by a knowledge of such excited states. Griffith & Orgel (44) have carried out calculations on the screening of cobalt nuclei in a number of complexes where the variations in screening constants are large and the nature of the appropriate excited states is fairly well known. Here they were able to get very good agreement with the experimental variations.

The variations of proton-screening constants have been determined for a large number of molecules and a certain amount of theoretical work has been done on their interpretation. The total range of proton chemical shifts is much smaller ($\sim 10^{-5}$) than for other nuclei, largely because of the smaller number of electrons in the immediate vicinity of the nucleus. Further, since the effects of local electron circulations on the hydrogen atom will be relatively small, the total screening of protons will be much more sensitive to the magnetic effects of neighbouring atoms. If the magnetic moments induced on other atoms are replaced by point dipoles, it can be shown that the resultant contribution to the proton screening will be proportional to the anisotropy of the local magnetic susceptibility of the other atoms (42, 43). In fact, if the neighbouring atom has a greater diamagnetic susceptibility along the X—H bond than perpendicular to it, the proton will experience increased screening. It has been suggested that this effect may be the cause of several apparent anomalies in proton chemical shifts which often do not

correlate with the expected electron density on the hydrogen atom. In particular, it is possible that the relatively high screening of protons in acetylene may be caused by magnetic anisotropy of the carbon atom and that the approximate equality of $\sigma$ in the series $CH_4$, $NH_3$, $H_2O$, and HF may be due to cancellation of variations due to changes of hydrogen electron density and changes of magnetic anisotropy on the central atom.

The theoretical interpretation of proton chemical shifts in aromatic hydrocarbons has also attracted some attention. The exceptional diamagnetic properties of these molecules, due to currents in the $\pi$-electron system, lead to reduction in the screening constants of protons in the molecular plane. Pople (45) suggested this as the origin of the lower screening of protons in benzene compared with ethylene and gave a simple calculation of the difference based on a simple ring model which is in reasonable agreement with observation. A similar theory was successful (46) in getting a semiquantitative interpretation of the chemical shifts between nonequivalent protons in polycyclic aromatic hydrocarbons such as anthracene and phenanthrene. In fact, the various protons in such a hydrocarbon can be used to explore the details of the ring currents which lead to the molecular diamagnetic anisotropy. This has led to some revival of interest in the quantum-mechanical theory of these currents which has been extended to the calculation of current in individual rings (27). McWeeny (47) has recently given a full extension of the London theory to the calculation of proton screening which gives rather larger effects than the semiclassical approach.

*Paramagnetism and electron spin resonance.*—If the electrons in a molecular system are not all paired, the electron spins can be oriented by an external magnetic field leading to paramagnetic polarization. In the corresponding quantum-mechanical treatment, there are a number of energy levels with a separation depending on the external magnetic field and the excess thermal population of the lower states leads to a resultant magnetic moment, the associated paramagnetic susceptibility being inversely proportional to temperature. In recent years, more detailed information about the states of unpaired electrons has become available from electron spin resonance experiments which investigate transitions induced between these states, so theoretical work in these two fields is best considered together.

In a classification of paramagnetic materials, it is simplest to separate systems in which spin-orbit interaction is negligible, so that the spin states of unpaired electrons are independent of spatial distribution. This is true to a high approximation in a number of simple organic radicals. For such systems, the molar magnetic susceptibility is given by the well-known expression $4N\beta^2S(S+1)/3k\ T$ where $\beta$ is the Bohr magneton and the total spin, $S$, is twice the number of unpaired electrons (the spin of each contributing $\frac{1}{2}$). If there is only one unpaired electron, there are two spin states which are separated by an energy gap, $g\beta H$, where $g$ is a numerical factor close to the free spin value 2.0023. This is the energy which is measured in an electron spin resonance experiment.

One of the most important diagnostic features of the electron spin reso-

nance spectra of simple radicals is the hyperfine structure due to the interaction of the unpaired electron with the spins of neighbouring nuclei. This gives detailed information about the distribution of "unpaired electron density" and has been the subject of a considerable amount of theoretical work. The interaction Hamiltonian between the electron spin **S** and the nuclear spin **I** has the form

$$2\beta\gamma\{[3(\mathbf{S}\cdot\mathbf{r})(\mathbf{I}\cdot\mathbf{r})r^{-5} - (\mathbf{S}\cdot\mathbf{I})r^{-3}] + (8\pi/3)\mathbf{S}\cdot\mathbf{I}\delta(r)\}$$

where $\gamma$ is the nuclear gyromagnetic ratio and $r$ the position vector of the electron relative to the nucleus. The first part of this Hamiltonian represents the direct dipole interaction between the magnetic moments and the second is the Fermi or "contact" term and involves the Dirac $\delta$-function. The dipole interaction part leads to hyperfine structure depending on orientation which can be observed in single crystals. In solutions, however, and in systems where sufficiently rapid tumbling and reorientation is taking place, the dipole part is effectively averaged to zero (48) and the hyperfine structure is determined by the contact term alone. For a single nucleus of spin $\frac{1}{2}$, the contact term gives a splitting of the spectrum into a doublet depending on the magnitude of the wave function in the immediate vicinity of the nucleus. For $n$ equivalent nuclei, there is a spectrum of $(n+1)$ lines with intensities proportional to the binomial coefficients of $(1+1)^n$. Since there are relatively few measurements on simple radicals in single crystals, most theoretical work has been concerned with the interpretation of observed values of contact terms.

If the odd electron is treated as an independent particle, the $\delta$-function in the Hamiltonian leads to a splitting proportional to the square of the wave function $|\psi(0)|^2$ at the nuclear position. However, it became clear that such a simple treatment was not altogether adequate when proton hyperfine structure was found in aromatic free radicals which were expected to be planar. If the odd electron is in a $\pi$-orbital its wave-function would be zero in the molecular plane and consequently at the nuclear positions. Weissman *et al.* (49) suggested that this was either due to zero-point out-of-plane vibrations or to configuration interaction. After the former hypothesis was shown to be quantitatively inadmissible by Venkataram & Fraenkel (50), successful semiquantitative estimates of the effect of configuration interaction were made by McConnell (51), Bersohn (52), Weissman (53), and Jarrett (54). These are all based on interactions between the $\pi$ electrons and the $\sigma$ electrons of the C—H bond. McConnell considered the problem of a three-electron system with a normal structure containing one electron in a $2p\pi$ carbon orbital ($p$) and the other two forming a bond between a $sp^2$ hybrid carbon orbital ($\sigma$) and the hydrogen $1s$ orbital ($s$). In the valence bond approach to this problem, three antisymmetrized products are possible corresponding to a total spin component $S_z = \frac{1}{2}$. These are

$$\phi_1 = a[p(1)\alpha(1)\sigma(2)\alpha(2)s(3)\beta(3)]$$
$$\phi_2 = a[p(1)\alpha(1)\sigma(2)\beta(2)s(3)\alpha(3)]$$
$$\phi_3 = a[p(1)\beta(1)\sigma(1)\alpha(2)s(3)\alpha(3)].$$

The two combinations of these corresponding to doublet states are $\psi=(\phi_1-\phi_2)/\sqrt{2}$ and $\psi_2=(\phi_1+\phi_2-2\phi_3)/\sqrt{6}$. The former corresponds to the usual valence bond structure with a C—H $\sigma$-bond, but a certain amount of the wave function $\psi_2$ is mixed with it in the optimum combination and it is this which gives rise to the hyperfine structure. The amount of mixing can be estimated by diagonalizing the matrix of the Hamiltonian. Weissman (53) showed that similar results could be obtained using molecular orbital theory. Extension of these theories to larger radicals (55, 56) indicates that the hyperfine interaction constant is expressible as a product $Q\rho$ where Q is the constant calculated for the three-electron model and $\rho$ is the $\pi$ odd-electron density on the carbon to which the proton is attached. $\rho$ is a quantity about which detailed predictions are made in quantum-mechanical theories of $\pi$-electrons and these have been compared with the electron-resonance data for a number of systems. In the naphthalene negative ion, for example, the spin density at the $\alpha$ proton is about three times that at the $\beta$-proton, in good agreement with theory (55, 57, 58). McConnell and Chesnut examined the theoretically predicted sign of Q and found it to be negative both in the valence-bond and molecular-orbital theories. Physically this means that if the resultant electron spin is aligned parallel to the applied field, there will be an excess of electrons with spin antiparallel to the field in the immediate vicinity of the aromatic protons and vice versa. Further development of the theory (59) also indicates that the $\pi$ odd-electron density itself may change sign from atom to atom. This could not be so in simple molecular orbital theory, of course, where the odd electron is treated separately, all others being paired; but valence bond calculations on simple radicals do give negative values. In the allyl radical, for example, molecular orbital theory predicts (59) a spin density of $+\frac{1}{2}$ on the two end carbon atoms and zero in the centre, whereas valence bond theory gives $+\frac{2}{3}$, $-\frac{1}{3}$ and $+\frac{2}{3}$. McConnell & Dearman (60) carried out similar valence-bond calculations on the perinaphthenyl radical and obtained $\rho$-values of $-0.176$ and $+0.321$ for the groups of three and six protons, respectively. These compare well with the "experimental" values of 0.098 and 0.325 for $|\rho|$ which are deduced from the hyperfine structure. Similar results are obtained if molecular orbital theory is modified by introducing configuration interaction. This has been discussed by Hoijtink (61), who has carried out such calculations for the naphthalene and biphenyl negative ions. For alternant radicals, Hoijtink shows that, if the effect of configuration interaction is treated as a perturbation, it will lead to negative spin densities on those atoms for which simple molecular orbital theory predicts no spin density.

Recently McConnell (62) has extended the theory of spin density further by writing the continuous (normalized) spin density $\rho(x, y, z)$ in the form

$$\rho(x, y, z) = \sum_{ij} \rho_{ij}\psi_i\psi_i$$

where $\psi_i$ are a set of orbitals and $\rho_{ij}$, the corresponding spin-density matrix. In particular, if $\psi_i$ are atomic orbitals in an LCAO approximation, the diagonal elements of $\rho_{ij}$ are the spin densities associated with the atomic

orbitals themselves, while off-diagonal elements correspond to the spin density in overlap regions which were not considered in the earlier treatments. McConnell applied the theory to the $\pi$-electrons of the allyl radical using the previously determined complete configurational wave function of Chalvet & Daudel (63) and obtained a spin density on the central atom of $\rho_{22} = -0.11$, intermediate between the predictions of valence bond and molecular orbital theory. In a later publication, McConnell applied the same method to the unrestricted selfconsistent molecular orbital wave function (in which all three electrons are permitted to occupy different orbitals). This wave function, which was obtained by Berthier (64), gives a large negative spin density on the central atom; but this is associated with the fact that the unrestricted self-consistent function is really a mixture of doublet and quartet states.

In addition to hyperfine structure from ring protons, effects are also observed from the protons of methyl groups as in methylated semiquinone ions and simple alkyl radicals (ethyl, propyl, etc.). In these systems, the presence of unpaired spin density on the methyl protons is attributed to hyperconjugation. The first quantitative theory of this was given by Bersohn (52) for semiquinone ions using a simple molecular orbital theory. Instead of trying to solve the problem in one step, he started by considering the aromatic radical ion and the $CH_3$ group separately and then investigated the effect on the singly occupied orbital of introducing a resonance integral $\beta^1$ between the two parts. Approximate calculations gave reasonable numerical agreement with experiment. A rather similar molecular orbital treatment of the simple aliphatic radicals ethyl, *iso*-propyl, and *tert*-butyl has been given by Chesnut (65). He found that the calculated coupling constants of the methyl group hydrogens were of the order of 15 to 25 gauss and do not decrease with the presence of additional methyl groups. Both these theories, being of the molecular orbital type, give positive spin densities on the hydrogen atoms. McLachlan (66) has applied valence bond theory to the problem and reached the same conclusion. His calculations gave a coupling constant of 28 gauss for the $CH_3$ protons of the ethyl radical.

*Electronic coupling of nuclear spins.*—Nuclear magnetic resonance spectra of liquids indicate that there is a coupling between nuclear spins $\mathbf{I}_1$, $\mathbf{I}_2$ which is in addition to their direct dipole interaction. This can be represented by the spin Hamiltonian $J\mathbf{I}_1 \cdot \mathbf{I}_2$ ($J$ being a constant) and is attributed to the coupling of the nuclear spins via the electrons of the molecule. Early theoretical interpretations did not give quantitative values of $J$ as large as those observed, but a full and successful theory based on the complete Hamiltonian for electron-nuclear interactions was outlined by Ramsey & Purcell (67) and developed in more detail in a later paper by Ramsey (68). Qualitatively the nuclear-spin coupling may be thought of as arising from secondary magnetic fields due to the electronic distortion by one nucleus acting on the second nucleus. The theory differs from that of nuclear screening in an external field, however, as the magnetic field of a nuclear magnetic

moment causes a redistribution of electron spins as well as electronic orbital currents.

The Ramsey theory is based on the division of the complete electron-nuclear interaction Hamiltonian into three parts: (*a*) the interaction of nuclear magnetic moments with electron orbital currents, (*b*) the dipole interaction between electron and nuclear magnetic moments, and (*c*) the "contact" term proportional to the properties of the electronic wave function at the nuclear positions. These coupling terms can be introduced by perturbation methods and energy changes calculated to the second order. Cross-terms involving different nuclei than give effective Hamiltonians of the required form $J\mathbf{I}_1 \cdot \mathbf{I}_2$ when averaged over orientations. Ramsey showed that the three types of interaction led to independent and additive contributions to the spin-coupling constant $J$. The complete expressions for these contributions involve the details of electronic excited states, but again these can be simplified if all excitation energies are replaced by an average value.

The simplest application of the theory is to the coupling between the two protons in the hydrogen molecule. Ramsey (68) carried out a calculation of the three terms and found that the contact term was dominant. Using a mean excitation energy, this contribution to $J$ is proportional to the probability of the two electrons simultaneously coinciding with the two nuclei. This can be evaluated using the accurate James-Coolidge wave function. With a value of 1.4 Rydbergs for the mean excitation energy, this gives a coupling constant of about 40 cycles per second compared with the experimental value of 43.5 cycles per second. By similar methods, Ramsey estimated the contributions of the dipole-dipole term and the electron orbital term to be about 3 and 0.5 cycles per second, respectively.

Approximate theoretical calculations of spin-coupling constants between nuclei in larger molecules can also be carried out using a mean excitation energy and a wave function for the ground state. Theories have been given using both molecular orbital and valence-bond wave functions for this purpose. The application of molecular orbital theory was first considered in detail by McConnell (69) who evaluated the matrix elements appearing in the Ramsey expressions using LCAO molecular orbitals and then simplifying by neglecting terms involving overlap between atomic orbitals and different atoms. When applied to protons, his expression for the contact term contribution reduces to the simple form

$$J_{NN'} = \frac{16}{9}\beta^2\gamma^2 h(\Delta E)^{-1}[\phi(0)]^4\eta_{NN'}^2$$

where $\beta$ is the Bohr magneton; $\gamma$, the proton magnetogyric ratio; $\phi(O)$, the value of the hydrogen 1*s* atomic orbital at its centre; and $\eta_{NN'}$, the bond order between the atoms $N$ and $N'$ as usually defined in LCAO molecular orbital theory. The other contributions are always small for proton-proton interactions, so that molecular orbital theory predicts that the coupling constants should be positive. Experimental values of both signs are found how-

ever, indicating that molecular orbital theory without configuration interaction does not always give an accurate picture of the relative electron distribution.

Rather more successful calculations of proton-proton coupling constants have been made on the basis of valence-bond wave functions by Karplus *et al.* (70). In particular they have considered the coupling between two protons bonded to the same carbon atom as a function of H-C-H angle. According to these calculations, $J$ decreases from $+27$ cycles per second to $+2.8$ cycles per second as the angle changes from 100° to 120°. For angles greater than 125°, the calculated value is negative. This is in approximate agreement with experimental data on methane and substituted ethylenes.

A number of coupling constants between protons attached to carbon atoms in aromatic rings have been determined and discussed theoretically. One possibility which has been examined in detail by McConnell (71) is that these are partly due to interactions via the mobile $\pi$-electron system. In simple molecular orbital theory, there is no direct contribution of this sort since the $\pi$-orbitals all have nodes through the protons if the molecule is planar. However, an indirect effect is possible if configuration interaction is included, by a mechanism related to that giving proton hyperfine structure in the electron resonance spectra of aromatic free radicals. Quantitatively, however, the magnitude of this contribution turns out to be relatively small. It seems likely, therefore, that the coupling constant between aromatic protons which are not very far apart is dominated by interaction through the $\sigma$-system.

Comparatively little work has been done on the theory of coupling constants involving nuclei other than hydrogen. The electron-orbital and dipole-dipole contributions may become considerably larger for atoms with atomic $p$ and $d$ orbitals. An approximate expression for the electron-orbital contribution can be obtained in terms of the anisotropy of the electronic screening tensors of the two nuclei involved (72), but application to some coupling constants involving fluorine nuclei suggests that the orbital part is still a relatively small contribution. Calculations of the relative importance of the dipole-dipole and contact terms are rather difficult owing to lack of knowledge of the behavior of higher atomic orbitals near the nucleus.

## General Molecular Quantum Mechanics

*Atoms.*—A number of papers have been published recently on wave functions and other quantum-mechanical properties of atoms and ions with one and two electrons. Coulson & Robinson (73, 74) have examined the solution of the wave equation for the hydrogen atom in spheroidal coordinates, one of the foci being at the nucleus. These coordinates are particularly appropriate for the perturbation caused by a point charge or dipole at the other focus, the corresponding wave functions being the correct zero-order ones to use in perturbation calculations. Several authors have considered various aspects of approximate wave functions for two- and three-elec-

tron atoms. Snyder & Parr (75) have had some success with variational functions for helium which are continuous but have only piecewise continuous derivatives. Difficulties associated with the calculation of the kinetic energy can be overcome, and such functions may be of use in more complex systems. Others have developed "open-shell" wave functions in which electrons of different spins are allowed to occupy different orbitals. Shull & Löwdin (76) showed that open shell calculations on helium-like ions allowed for an appreciable amount of radial electron correlation and gave a significant improvement in the energy. These results have been extended to higher atomic numbers and to three-electron systems by Hurst and co-workers (77). They found the energy improvement by replacing closed shell with open shell calculations decreased with an increasing atomic number. The open-shell calculated energies for He and $He^-$ were equal within the error of the calculation, indicating zero electron affinity for helium. Since the remaining error in three-electron calculations is likely to be the greater, this led Hurst *et al.* to suggest that helium has a slightly-positive electron affinity.

An important tabulation in connection with the calculation of atomic valence state energies has been published by Companion & Ellison (78). They give the expansions of atomic state functions in terms of determinants over atomic orbitals for all possible structures involving *s*- and *p*-electrons and illustrate the application to the calculation of promotional energies.

*Diatomic molecules.*—Several new approximate wave functions for the hydrogen molecule have been proposed during the past year. Joy & Parr (79) have calculated a seven-term one-centre wave function centered at the molecular mid-point using Slater orbitals with nonintegral principal quantum number (80). This function has sufficient flexibility to give a binding energy of 4.32 ev (experimentally, 4.75 ev) and suggests that other molecules such as methane should be amenable to attack by this method. An important development in the theory of the excited states of the hydrogen molecule is the different atomic screening constants in the LCAO forms of the bonding and antibonding molecular orbitals $\sigma_g$ and $\sigma_u$. This has been investigated independently by Huzinaga (81) and by Phillipson & Mulliken (82). Radical improvement is obtained in the computed energies of the singlet and triplet states arising from the configuration $(\sigma_g\,\sigma_u)$. This and the application of the same method to other systems by Huzinaga suggests that antisymmetrical wave functions built entirely from molecular orbitals may be better than had hitherto been supposed. Barnett, Birss & Coulson (83) have investigated electron correlation in the hydrogen molecule by evaluating the mean distance and the mean inverse distance between the electrons using various wave functions. They found that a Heitler-London wave function exhibits more correlation and a molecular orbital function less correlation than a covalent-ionic function.

There has been considerable progress in the calculation of approximate wave functions for diatomic hydrides during the past year. Complete valence bond calculations based on $1s$, $2s$, $2p\sigma$ and $1s_H$ orbitals have been carried

out for LiH and $BeH^+$ by Miller *et al.* (84). For LiH, the calculated energy was −216.95 ev (experimentally, −219.71 ev) and the dipole moment 6.04 D (hydrogen negative). Ormand & Matsen (85) have repeated the original calculation of Knipp on LiH using spheroidal coordinates and obtain −217.13 ev for the energy and 5.57 D for the dipole moment. Self-consistent linear combination of atomic orbital calculations based on the Roothaan procedure (86) have been carried out by Krauss (87) for CH, $CH^+$, NH, OH, and FH. Slater atomic orbitals were used throughout. Krauss reported calculated values for the ionization potentials, excitation energies binding energies and dipole moments. Boyd (88) has made a similar calculation on NH. An extensive study of the OH radical has been made by Freeman (89) using Hartree-Fock atomic orbitals. He discussed configuration interaction based both directly on atomic orbitals and on SCF molecular orbitals. No single valence-bond configuration was found to give any binding and a single molecular orbital configuration gave about 25 per cent of the observed binding energy. The inclusion of configuration interaction using LCAO SCF orbitals as basis gives little further improvement.

A number of semiempirical methods have been proposed for correcting the major deficiencies of nonempirical calculations. Moffitt's original proposal (90) to obtain the atomic part of the molecular energy from atomic spectral data (the method of "atoms in molecules") has been refined by Hurley (91) and Arai (92) who have allowed for atomic distortion in molecular fields. Calculations including corrections of this sort have been reported during the past year for $Li_2$ by Arai & Sakamoto (93) and for a series of diatomic hydrides by Hurley (94, 95).

*Polyatomic molecules.*—The a priori calculation of electronic wave functions for polyatomic molecules and radicals is made more difficult by the complexity and number of the multicentre integrals involved, but nevertheless, several such calculations have been performed. Higuchi (96, 97) has applied the LCAO SCF molecular orbital method to the series NH, $NH_2$, $NH_3$ and also to the methyl radical assuming it to be planar. Recently he has refined the latter calculation (98) by including the carbon 3*s* atomic orbital in the set of basic functions. Approximate LCAO SCF molecular orbital calculations have also been made for diborane (neglecting inner shells) by Yamazaki (99). These suggest that the net charge on the bridge hydrogens is negative while that on the terminal hydrogens is neutral.

New one-centre wave functions for $CH_4$ have been calculated by Mills (100). In early work on this topic (16) it was assumed that the potential field of the four protons could be replaced by a charge +4e smoothed over a spherical surface. Mills has refined this calculation, obtaining the optimum Hartree-Fock determinantal wave function, and has also considered the effect of the leading nonspherical term in the spherical harmonic expansion of the proton potential field. In a second paper (101), he has calculated absorption intensities of infra-red active vibrations by a perturbation calculation based on these wave functions. Although the calculated values are

larger than those observed, the qualitative features and sign relationships of the dipole moment derivatives are significant.

Kimball & Trulio (102) have carried out LCAO molecular orbital calculation (with configuration interaction) on the linear symmetric $H_3$ complex. This is based on a set of five 1*s* functions with centres equally spaced along the line of nuclei, but the spacing is varied independently of the internuclear distance [as with the $H_2$ calculation of Gurnee & Magee (103)]. The calculated binding energy (relative to three separate hydrogen atoms) was 72.4 kcal./mole, rather less than the best available value of 80.3 kcal./mole (104).

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# ELECTRONIC SPECTRA OF ORGANIC COMPOUNDS[1]

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## GENERAL

This review will concentrate on the organic compounds—in general, conjugated systems—that give near-ultraviolet and visible spectra. Even in this limited field, the literature on the spectra or closely relevant to their interpretation amounts to over 500 papers from 1 December 1957 to 1 December 1958. This has made it necessary to curtail most of the direct references to earlier work.

It was a doubly black year for molecular spectroscopy in the loss of Jerome W. Sidman at the age of 28 and William Moffitt at the age of 33. Sidman's was the fastest-rising experimental star in America, and Moffitt's was the fastest-rising theoretical one. A complete list of their publications is given in the bibliography; it is short but golden, and a good introduction to the best current work in this field. Sidman's 23 papers (1 to 14), packed into three years, decided the assignments of numerous excited states crucial to the validation of theoretical interpretations. Nearly half of Moffitt's 40 papers (15 to 32) were also in the last three years; each was an elegant gem. His major theoretical advances include the method of atoms-in-molecules (16, 17, 19), his work on optical rotation (23, 24, 26), and on the Jahn-Teller effect (25, 28, 29, 30); and his perturbation method relating the intensities and wavelengths of the spectra of different aromatics (20), a theory whose importance in this field is comparable, say, to the importance of the complete theory of the Zeeman effect in interpreting atomic spectra.

### Books, Reviews, Symposia

*New books.*—The new journal in 1958 is *Molecular Physics*, edited by Longuet-Higgins and van der Waals. *Advances in Chemical Physics* begins a series of annual review volumes, edited by Prigogine. Kasha & Kasha, *Molecular Electronic Bibliography* (33), is a complete list of the publications through 1955 of Coulson, Eyring, Heitler, Herzberg, E. Hückel, Hund, Hylleraas, Jordan, Lennard-Jones, London, Mulliken, Pauling, Penney, Slater, Sponer, Teller, and Van Vleck. The *Dictionary of Values of Molecular Constants, III, Second Part*, by Coulson & Daudel (34), has tables of molecular-orbital coefficients and energies for 32 more conjugated systems.

*Spectra.*—There are some 25 reviews related to organic spectra or their interpretation. The Herzberg review (35) emphasized the spectra of di, tri, and tetraatomic molecules. Stevens (36) has reviewed the fluorescence and quenching kinetics of complex aromatics in vapor phase.

*Electronic structure.*—Reviews have been prepared on: the theory of electronic structure by Kotani & co-workers (37); valency bonding in nitro-

[1] The survey of the literature was completed December, 1958.

gen compounds by Orville-Thomas (38); molecular orbital theory and aromatic spectra by Longuet-Higgins (38a); aromatic theory and carcinogenicity by Daudel (38b); free valence in conjugated organics by Pullman & Pullman (39); the electronic states of molecules and ions in crystals by McClure (40); and steric hindrance by Ingold (41).

In electron distribution, "directional" or localization effects not given by symmetry or going beyond symmetry—such as "banana" orbitals in ethylene, and "bent" nonbonding orbitals in HF—are stressed in several reviews. Pople (42) gives the "equivalent-orbital" approach, and Linnett (43) uses it to treat the shapes of excited species. Dickens & Linnett (44) treat electron correlation and its chemical consequences, remarking that for the ground state of ethylene "maybe the $\sigma/\pi$ description has been overstressed." Somewhat different approaches to electron correlation were given earlier by Daudel, Brion & Odiot (45) and Kuhn (46). Similar directional effects are manifest generally in the alternating maxima and minima of electron density in ground and excited states (47), even in sigma-electron systems (48).

*Related data.*—Bond lengths and angles were reviewed by Stevenson & Ibers (49), who assert that there are surprisingly large uncertainties in the measurements. The relation of electron density to Hammett substituent constants and reaction mechanisms was reviewed by Taft, Deno & Skell (50); and especially for aromatic nucleophilic substitution reactions, by Bunnett (51).

*Special molecules.*—The review on carbonium ions by Bethell & Gold (52) treats cogently the spectral evidence on bridged versus nonbridged structures. Electron-deficient molecules, mostly boron hydrides, are reviewed by Longuet-Higgins (53).

*Special states.*—One of Sidman's last papers was his comprehensive review (12) on n-$\pi$ transitions in carbonyls, nitrosos, nitrates, and azaaromatics. The triplet state has been reviewed by Reid (54) for chemists and biochemists, and Ross (55) has given a more mathematical survey of spin-orbital coupling in atoms and molecules for physical chemists.

*Optical rotatory power.*—The review by Kuhn (56) emphasizes the physical relation between molecular absorption spectra and optical rotatory power. [And see (32).] The important biological applications of the Kirkwood-Moffitt theory (23, 24, 26) of optical rotation of macromolecules containing helically arranged polypeptide or aromatic absorbing groups, are foreshadowed in the earlier review by Kauzmann (57).

*Structure and spectra of complexes.*—The earlier review of "crystal field theory" by Moffitt & Ballhausen (21) is now matched from the other Cambridge by a review of "ligand field theory" by Griffith & Orgel (58). Relative affinities of ligand atoms for acceptor molecules and ions are tabulated by Ahrland, Chatt & Davies (59); absorption and fluorescence of ions in crystal fields, by Runciman (60). The treatment of complexes here will be limited to the cases of large organic ligands or a clear relation to organic spectra.

Donor-acceptor molecular complexes of the 1:1 type, which frequently involve organic molecules and have strong spectra, are reviewed by Briegleb (61) and McGlynn (62); the latter has a bibliography of 250 papers. Hydrogen-bonding is reviewed by Cannon (63).

*Symposia.*—The International Conference on Spectroscopy Colloquium on Ultraviolet Absorptiometry was held in Amsterdam, in May 1956 (64). A conference on theory and experiment in the problem of chemical binding was held by the Bunsengesellschaft at Kiel, 30 May to 2 June 1957 (65). A symposium on the structure and reactivity of electronically excited species took place at Ottawa, September 1957 (66); and a colloquium on the calculation of molecular wavefunctions at Paris, 30 September to 6 October 1957 (67). A New York Academy of Sciences conference on photo-reception was conducted at New York City, 31 January to 1 February 1958 (68); a conference on hyperconjugation at Bloomington, Indiana, June 1958 (69); a Chemical Society Symposium on steric effects in conjugated systems at the University at Hull, July 1958 (69a); a panel meeting on the correspondence between concepts in chemistry and quantum chemistry at Valadalen, Sweden, in August 1958 (69b), with some 20 theorists discussing atoms-in-molecules, hindered rotation, conjugation and bondlengths, and the problem of theoretical prediction. The twelfth annual Ohio State University symposium on Molecular Structure and Spectroscopy at Columbus, Ohio, 16 to 20 June 1958, had five sessions on electronic structure and spectra, mostly of conjugated molecules, but these papers are not published together. Individual papers from these symposia will be mentioned below under their appropriate subjects.

*Note added in proof:* Three important volumes arrived too late for coverage in this review: The Proceedings of the Third Conference on Carbon, Buffalo, N. Y., July 1957 (69c), with papers on electronic properties, magnetism, and conductance of large aromatics and related compounds, by Pullman, Matsen, Coulson, Pacault, Akamatu, Ubbelohde, Lyons, Ingram and others; the Chemical Society Symposia in Bristol, 1958 (69d), with papers by Baker and McOmie on the cyclobutadiene problem, by Reid on azulene, by Coulson on conjugation, and by Roberts on benzyne intermediates, and with papers by Longuet-Higgins, Ingram, Pople, Dewar, Duchesne, and others on electron and nuclear resonance; and a volume of Tables of Interatomic Distances (up to 1955), compiled by Sutton (69e).

## General Theory

*Basic electronic formulation.*—The systematics and symbolic formulation of the chemical bond are examined by W. Hückel (70); the tetrahedral carbon atom by Raman (71); the valence-angle problem in molecular orbital theory by Artmann (72); and excited states and shapes of $CO_2$, $C_2H_2$, HCN, etc., by Mulliken (73). The free-electron and one-dimensional approaches developed for conjugated systems are proving their value also for sigma bonds [Kuhn & co-workers (73a); Arnold (74); Frost (75); Barrow (76); Lippincott

& Dayhoff (77); Platt (47, 48)]. The same is happening with semiclassical electron density models [(47, 48); Bauman (78)]. Lakatos (79) has computed bond polarities; Earl (80) regards the bond as a "vector quantity"; and polarity has a central role in the new Parks & Parr theory of "separated electron pairs" (81). Kołos (82) has re-examined the assumptions of the Pariser-Parr method, and Simpson (83) has re-examined the problem of the Fermi hole in Hückel theory.

The wave-function distributions in saturated organics have been calculated by Del Re (84) and in cyclics by Handler & Anderson (85). They are related to substitution reactions by Bykov (86). The distribution in multiple bonds is given by Sinn (87) and Bykov (88).

Wilson's thought-provoking tabulation of internal-rotation barriers (89) showed that these barriers could not be due to any direct repulsions and needed theoretical re-examination. This has been related now to *d* and *f* mixing by Pauling (90) and, contrariwise, to a "principle of minimum bending" by Eyring & co-workers (91). It is also related to the spatial separation of electron density maxima (47, 48). [See also (69b.)]

*Conjugated systems: Kekule structures.*—The mathematical identity between the first-order electronic distributions and stabilities given by (*a*) simple molecular-orbital theory (either in the linear-combination-of-atomic-orbitals or the free-electron form) and those given by (*b*) single-sign resonance theory (where all principal Kekulé structures have the same sign), was established for odd alternant hydrocarbons and linked combinations of them in the classic papers of Longuet-Higgins (92) and Dewar & Longuet-Higgins (93). The identity holds for some low excited states as well as the ground state (47). Ham (94) has now proved a similar identity between (*a*) new bond orders obtained from the molecular determinants by Ruedenberg & Ham (95) and (*b*) the Pauling bond orders for even alternant hydrocarbons. Ruedenberg describes molecular topology as the mathematical "generatrix of bond orders"; and he also discusses a program for the elimination of semiempirical elements from pi-electron theories (96). Moffitt has published a simplification in factoring the secular equations of alternants (27), following Ruedenberg & Scherr (96a) and Longuet-Higgins (92). A useful transformation of the determinants, related to the "method of polygons," has been given by Samuel (97).

Clar, Kemp & Stewart (98) have illustrated the role of Kekulé structures in chemical stability. That structures of opposite sign lead to instability (triplet ground state) is supported by the repeated failures to prepare cyclobutadiene [Longuet-Higgins & Orgel (99)] and a new disproof of a supposed derivative (100). The benzene structures have been discussed by Earl (101), and structures with fractional bond orders by Finkel'shtein (102).

*Conjugation in polyenes?*—The Kuhn alternation of single and double bonds necessary to explain long-polyene spectra (37)—directly contradicting the equivalence of bonds or mixture of resonance structures long assumed by theorists—considerably damaged the importance of conjugation or reso-

nance for the ground states of those even-atom hydrocarbons for which only one unexcited structure can be written. Dewar & Wulfman (103) have now shown theoretically that the most probable spatial arrangement of the pi-electrons in polyenes is one in which those of the same spin lie almost exactly at the centers of the classical double bonds. Dewar (103a) and Dewar & Schmeising (104) have dealt conjugation a further and more serious blow by showing that most of the original arguments for resonance in such cases were faulty, the crucial ones being based on a failure to distinguish between the atomic radius and energy of bond formation of an $sp^3$ carbon atom and those of an $sp^2$ atom. When these distinctions are made, it appears that heats of formation and bond lengths can be predicted in even-atom chains without considering resonance at all; and even in benzene, the effects of resonance between structures become secondary. Important contributory evidence is that the new value of 1.337 A for the C=C bond length in ethylene (105 to 107a) is identical with that in butadiene (108); and the C—C bond length of 1.48 A in the latter and in acetonitriles (109) represents no shortening of the Dewar $sp^2$—$sp^2$ single-bond distance; and the benzene C—C length is just halfway between the new values for single and double C—C bonds with four neighbors (107a). [See also (69b).] [But Cook (110) discusses the effects of twisting on such a single bond length between two double bonds.]

*Hyperconjugation.*— If conjugation goes, where does that leave hyperconjugation? Mulliken (111) has taken issue with the Dewar criticism in a paper on hyperconjugation. "Isovalent hyperconjugation" is proposed as a separate type, like "isovalent conjugation" (two equivalent resonance structures), in two other papers (112, 113). Other recent papers on hyperconjugation are by Morita (114), Lei (115), Beech (116), and Beck & Beck (effect on molar volumes) (117). It was not found in malonitrile (118) but may be important in radicals [(112); McLachlan (119)].

*Wavefunctions for conjugated systems.*—Resonance in aromatics is discussed by Hückel (120); the pi-electron in aromatic chemistry, by Longuet-Higgins (121) and by Dewar (122); negative-ion electron distributions and reactivities, by Hoijtink (123); energy levels from benzene to graphite, by Coulson (124), and their change with deformation in aromatics (125); and a novel type of aromaticity, by Craig & Paddock (126). The role of atomic valence states in the benzene energy calculations is examined by Hurley (127). The theory of the spectra is related to the molecular orbital treatments of ionization potentials (128), polarographic potentials (129), oxidation potentials (130), electron densities and bond lengths (131), perturbations (132), chemical reactivities (133 to 136), properties of butadiene (137), and even molar volume (138). Odd-membered ring systems have been treated (139, 140, 141), the triphenylcyclopropenyl cation (142) and some radicals (143).

In conjugated systems, theoretical wavefunctions and spin densities (which can be negative!) are being checked by electron magnetic resonance

measurements, as discussed by McConnell & co-workers for radicals (144, 145, 146) and metal aromatic complexes (147). The observations for aromatic ions, and their relations to spectra, are discussed by Tuttle & Weissman (148); by de Boer & Weissman (149); triphenylmethyl, by Adam & Weissman (149a); other ions by Mackor & co-workers (150); and by Hoijtink (151). For some compounds, the molecular orbital wavefunctions give excellent results; for others (odd alternants), the resonance theory is better (144, 146); many puzzling points remain.

Pauling ring currents ("free-electron") in aromatics have had a renewed vogue in the calculation of nuclear magnetic resonance [Pople (152); McWeeny (153); Johnson & Bovey (154)] and the diamagnetic shielding effects of solvents (155) as well as the diamagnetic anisotropy of benzene (156, 157, 158).

Other approximations for the electronic wavefunctions include a united-atom theory of large molecules by Chen (159); and free-electron calculations by Kuhn [for chain molecules; (160, 161)] and by Gołębiewski (162) and Bán (163, 164). [Kuhn also seems to have settled the old controversy over the strengths of transitions from an orbital filled with two electrons (165).] Free-electron estimates have been made (166) of the absorption by "random molecules" or assemblages of atoms in interstellar space, with somewhat surprising results as to the sizes of such "dust particles" needed to account for interstellar reddening.

Burawoy (167) has tried to relate to modern theory his valuable classification of spectral types, whose validity was denied for so many years. Jennen (168) has extended his interpretations. The early supposition of Baly and others, that ultraviolet frequencies were regular harmonics of infrared frequencies, is still being refuted (169); but is giving way to more subtle and useful relations showing the parallel effects of electronic displacement on force constants and transition energies (170, 171, 172).

*Nomenclature.*—Kasha & Platt (173) have made a strong plea for the adoption, by theorists and experimental spectroscopists alike, of a systematic nomenclature for the states and transitions of organic compounds. The literature is cluttered with numerous primitive and private terminologies, both empirical and theoretical—"primary," "secondary," and "benzenoid" bands; A-, B-, C-, and E-bands; R-bands and K-bands; $\alpha$-, $\beta$-, and $p$-bands; *cis*-bands; S and T, T′, T″ states; N, V, and T states and corresponding transitions; $n_1$, $n_2$, $\pi_1$, $\pi_2$, $\phi_1$, $\phi_2$ states and transitions; and so on. These all represent useful partial classifications, but with 500 new papers per year, the babble of tongues will engulf us, unless we all agree to use some simple symbolism for these regularities that is complete and consistent with theory. These authors urge general adoption of essentially the terminology proposed earlier (12, 174), which has also been taken up by a few others. This is the terminology of $^1L_a$, $^3L_a$, $^1L_b$, $^3L_b$, for particular low excited states of aromatics and their derivatives; $^1Q$, $^3Q$ for the low porphine states; $^1U$, $^3U$, $^1W$, $^3W$ for particular states of $n\pi$ excited configurations of heteroconjugates; $^1A$, $^1B$,

$^1C$, . . . for the ground state and low "classical-oscillator" states (strong transitions); and so on. These recommendations are consistent with the 1955 Mulliken Report on Notation for Polyatomic Spectra (175), especially Sections 3(a)(4) and Recommendation 15; but the sense of urgency in the large-organic field is 1500 papers keener now.

## INDIVIDUAL COMPOUNDS

*Vacuum ultraviolet.*—Standard wavelength tables for the vacuum ultraviolet are given by Milazzo (176) and a useful reprint of the Rydberg term tables by Sutcliffe (177). The higher ionization potentials of $CO_2$, $CS_2$, COS, and $N_2O$ were measured by Tanaka, Jursa & LeBlanc (178). The absorption and ionization coefficients of ethylene oxide by Lowrey & Watanabe (179). The far ultraviolet spectra of saturated hydrocarbons have been measured (180); Rydberg series in $CH_3F$ and $CHF_3$ (181); other fluorine compounds (182); hydrogen and benzene (183); and alcohols (184). Pickett & co-workers have measured chlorocyclopropane (185) and other small-ring systems (186), relating transition peaks to dipole-moment deviations; Wilkinson (187) has made detailed vibrational analyses of the Rydberg series of acetylene and deuteroacetylene. Heylen (188) has related the electric strength of gases to their ultraviolet spectra.

Small complex chromophores studied at longer wavelengths include ethylene sulfides (189); polyvinylalcohol (190); and organosilicon compounds (191).

*Small double-bond systems.*—Another molecular orbital treatment of the $^1B$-$^1A$ and $^3B$-$^1A$ transitions of ethylene (old N-V and N-T) has been given by Barriol & Regnier (192), and Liehr (193) has computed potential curves. Serré (194) treated the states of acetylene; and Simonetta and co-workers (195), those of vinyl chloride.

By electron diffraction, Bastiansen & co-workers (196) showed that cyclo-octatetraene—nonplanar, with four unconjugated ethylenes—has the tub form ($D_{2d}$), with the new ethylenic C=C bond length [see also (197)]. Chloroprene has also been examined (198).

The spectra of isocyanate and isothiocyanate have been studied (199); the perfluoronitroso-alkanes and nitro-alkanes (200); the nitrites and $N_2O_4$ (201, 202). Coulson & Duchesne (203) and Coulson (204) describe $N_2O_4$ as containing a "new type" of chemical bond.

HCOOH has been shown to be planar by microwave studies (205). The spectra of fatty acids (206) and unsaturated acids (207) have been remeasured. (Peptides will be reviewed with the biological compounds.) The spectra of phosphoric acid amido-derivatives have been measured (208), and numerous sulfides and sulfones (209 to 213). The five-ring systems whose spectra and structure have been studied include furan [vacuum region (214)]; pyrroles (215, 216); thiophenes (217, 218) [molecular refraction (219)]; cyclic disulfides (theory) (220); and selenophenes (221). Cyclohexadiene has been measured again (222).

## Aromatics

*Benzene.*—The bond lengths in benzene were discussed by Cyvin (223). The theory of vibrational-electronic interactions and intensities in the 2600 and 2100 A transitions under various assumptions is given by Liehr (224, 225). The shifts of these transitions with pressure in various gases (some to the red, some to the blue!) were measured by Robertson & Babb (226) and Robertson, Babb & Robinson (227) and have been predicted theoretically by Polansky (228). The crystal spectra of benzene and naphthalene have been calculated (229).

*Substituted benzenes.*—The perturbations of these benzene transitions by the inductive and conjugative effects of various chemical substituents were treated theoretically by Goodman & Shull (230) with an approach similar to Moffitt's (20). Goodman & Frolen (231) treated the spectra and spectroscopic moments of haloanisoles and concluded that iodine and bromine utilize their open shell orbitals in conjugation. Polansky (232) applied a theory of wavelength shifts to methylbenzenes. Others have also studied the influence of substituents (233), the correlation with reactivity constants (233a), the electron donor properties of the neopentyl group (234), and steric deformations in halobenzenes (235). The crystal spectra of benzyl and bibenzyl have been calculated (236). The structure and spectra of nitro compounds were computed by McEwen (237). The structure of benzoic acids has been calculated with respect to their diamagnetism (ortho effects) (238) and their biochemical auxin activity (239).

On the experimental side, the spectra of halobenzenes have been analyzed (240). Albrecht (241) has made detailed polarization studies of the paraphenylenediamine spectra by the interesting method of polarized photooxidation. Schnepp (242) has studied induced moments in the crystal spectra of polychlorobenzenes. Other benzene studies include various derivatives (243); nitrobenzenes, benzaldehydes, and anilines (244); nitrostyrenes (245); terephthalates (246); the tautomerism of sulfanilamides (247); and complex chlorophenyls (248); with applications to analysis (249, 250). The effects of acidity on methylbenzene spectra have been studied (251); other pH and ortho effects (252); and the spectral changes in hexamethylbenzene under a phase transition (253).

A theoretical interpretation of the effect of twisting on the ground and excited states and spectra of ortho-substituted dimethylanilines has been given by McRae & Goodman (254). The effect of twisting on the "conjugation signs" has been discussed (255); and some new spectra of these molecules have been measured (256). The roles of induction and resonance in twisted phenylacetates and phenylacetanilides have also been inferred from infrared frequencies (257). Wepster & co-workers (258) measured the spectra and basicities of many twisted aromatic amino-, acylamino-, and nitrocompounds and were able to account for the intensities with the vectorial method. [See also (69a).]

*Larger hydrocarbons.*—The proton resonance spectra of condensed ring systems (259) and those of azulene and acepleiadylene (260) bear on the electron density question. A self-consistent-field treatment of naphthalene is given by Kolboe & Pullman (261), and the levels and phosphorescence of diphenyl are computed by Iguchi (262) and Stewart (263). The nucleophilic characters of methylbenzanthracenes have been related to their ionization potentials by Nakajima (264). Overcrowding distortions in aromatics have been computed by Ali (265).

As for crystal spectra [see (229)], the optical theory of the measurements has been examined (266); the group splittings have been calculated for durene, ovalene, and phthalocyanine by Lyons (267); toluene, dibenzyl, diphenylmethane and biphenyl have been studied by Coffman & McClure (268); anthracene and pyrene absorption and fluorescence by Ferguson & Schneider (269); and thin films of naphthalene and anthracene by Perkampus (270).

Using the polarized fluorescence method, Williams (271) has challenged the theorists by showing that the relative polarizations of the transitions of anthracene agree with the predictions while those of pyrene and perylene do not. Alkylphenanthrenes have been studied (272), and the interesting cyclophanes (273, 273a). Reid (274) has compared the spectra of perinaphthyl radicals and ions with those of the odd 5-6-6-6 ring system, cyclopenta(a)-perinaphthindene, and its derivatives. A cycloheptabenzindene has been studied (275); and triphenylazulenes (275a). Some weak aromatic spectra have been measured more carefully (276).

*Saturated hetero derivatives.*—The spectra studied include hydroxydiphenylamines (277); phenylthiophenes (278); sulfur-containing naphthalenes (279); thionaphthenes (280); skatoles (281); nitroindoles and chloroindoles (282); benzothiazoles (283); carbazoles (284); benzocarbazoles (285); aryldihydrophenanthrenes (286); the characteristic transitions of various heteroaromatics (287); and interesting boro and azaboro compounds isoconjugate with the aromatics (288).

*Carboxyls and amides.*—Regularities have been studied in the spectra of hydroxycinnamic acids by Sutherland (289); and in aryl alkali amides by Döller, Förster & Renner (290, 290a). Kinetic studies have been made on heterocyclic amides (291). Ionization and spectra have been studied for salicylaldoxime (292) and thiohydantoins (293). Arcoria & co-workers (294) have examined the arylphthalimides.

The spectra and basicity of azoazulenes and of aminoazulene and its conjugate acid have been studied by Heilbronner & co-workers (295).

The solvent shifts of sulfones (212) permit dipole moment inferences. The spectra of other complex ring compounds include sulfenic acids (296); nitrodiphenylmethanes and similar systems (297); benzylidenetetralone (298); naphthalene picrate (299); benzoselenadiazoles (300); and a phenothiazinemaleate (plegicil) (301).

## Aza-Aromatics

Bak & co-workers (302) have determined the structure of pyridine from microwave spectra, and Cumper (303) has discussed the structures of other heterocyclics. Hameka & Liquori (304) have treated the dipole moments of azines. The resonance energy of acridine has been discussed (305), and the chemical evidence for "electronic transmission" through the chloroquinolines (306). Pullman & Effinger have treated theoretically the mechanism of aza-aromatic radical reactions (307); Nakajima & Pullman, the basicity of aza-aromatics and purines (307a).

*Theoretical.*—Anno & Sadô (308) found that the Pariser-Parr method predicts the pyrazine singlets too high, even with doubly-excited configuration interaction, unless the s-character of $sp^2$ N-orbitals is reduced to about 0.1, in line with the early Kasha conclusion. Murrell (309) computed the benzene N-heterocyclic spectra and the effects of acid on azaaminoaromatic spectra (309a); Mason (309b) interpreted the n-$\pi$ spectra in pyridazine; and Mataga & co-workers have computed azanaphthalenes and azaanthracenes (310, 311), and pyridinium ion (312).

*Spectra.*—[See (288, 295).] Tsubomura (313) studied the spectra of 4-methoxypyridine, 4-pyrone, and their salts. Hirt (314) studied the vapor spectra of pyrazines, and Hirt & Schmitt (315) the spectra of oxotriazines and their acyclic analogues. The substituent effects on quinolines have been examined (316); Bliznyukov & co-workers (317) studied the spectra and structure of substituted quinolines (antimalarials) and acridine; and others have done aminoquinolines (318) and aminoacridine (319). Zanker & Schiefele (320) have confirmed the assignment of the lowest singlet of the deeply colored acridines, by the method of substituent perturbation. The benzotriazines and naphthotriazines have been studied (321).

The pH effects on quinoxaline spectra have been probed by Tombácz (322); on 1,8-napthyridines by Skoda & Bayzer (323); and on hydroxyacridines and hydroxyphenazines by Perkampus & Rössel (324). Hata (325) studied the spectral changes in forming N-oxides of pyridinemethanols and pyridinecarboxylic acids; the N-oxides of other heterocyclics (326) and their hydrogen bonding effects (327) have been studied. Rao & co-workers studied the electron-withdrawing effects of the nitrogen groups on triazole (328) and tetrazole spectra (329). Other studies include naphthotriazoles (330), and indazoles (331). The absorption and pH effects (331a) and photodecomposition (332) of diazobenzenes have been examined. Tautomerism has been investigated in diazoketones (333) and in N-heterocyclichydroxy compounds (334).

## Carbonyl Compounds

Ketones and quinones (and nitroso compounds) form a separate class because some of their n-$\pi$ transitions (Burawoy's "R-bands") are almost invariably lower than any $\pi$-$\pi$ transitions. (In aza-aromatics and carboxyls and nitro compounds, this happens sometimes but not always.) As Sidman emphasizes (12), several different low $^1U$-$^1A$, $^3U$-$^1A$, $^1W$-$^1A$, and $^3W$-$^1A$ transi-

tions with various polarizations and intensities are to be looked for in hetero and polyhetero compounds; and one of his last interests was in straightening out these assignments (6, 10, 12).

For formaldehyde, Pople & Sidman (11) calculated successfully the $^1U$-$^1A$ intensity (2900 A). The nature of the upper state was examined by Robinson & DiGiorgio (335, 336). Molecular orbital treatments were given by Anno & Sadô (337), Brown & Heffernan (338) and Sender & Berthier (339). Matsen (340) discussed carbonyl intensities in his useful review on interpretation of spectra. A study of wavelength shifts in solutions was made by Maroni (341). The effects of substituents have been treated (341, 342). The relations of these spectra to bond constants and redox potentials are discussed by Brück & Scheibe (343). The states of camphorquinone have been studied (344); the spectrum of a norcamphor (344a); propargyl aldehyde (345); the stereochemistry of large-ring ketones (345a); aminoketones (345b); and the states of glyoxal (346) and its solution spectra (347) and those of *bis*-$\beta$-diketones (348).

*Aromatic ketones and quinones.*—Pullman & Diner have treated the electronic mechanism of radical reactions in quinones (349) and the electronic characteristics of polyquinones (350). The bond orders and stability of cyclopentadienone and indenone have been computed (351); and of naphthoquinone (352). Anno, Matubara & Sadô (353) have calculated the states and vibrational frequencies of benzoquinone by the Pariser-Parr method and Kuboyama (354) has explained the similarity among the $\pi$-$\pi$ transitions, and the sequence of n-$\pi$ energies in the benzoquinones, naphthoquinones, and anthraquinones. Labhart (354a) was able to interpret the spectra of anthraquinones using the vectorial method.

Spectra include those of cyclohexadienones ("chinol" acetates) (355); steric effects in duryl ketones (356); ring-chain tautomerism in benzoylpropionamides (357); the absorption and luminescence of various aldehydes, phenones, fluorenone, and anthrone (358); the spectra and chemistry of other acylanthracenes and ketoanthracenes (359); and the spectra and photochemistry of aminoanthraquinones (360). Kokubun has studied the absorption and fluorescence of acridone (361), and solvent effects (362); and the flavones (363, 364), and flavonols (365), and the photodimerization of a pyrone (365a) have been investigated.

## Chains and Dyes

*Alternating-bond chains.*—[See (103, 104).] Huzinaga & Hasino have a new formula for polyene spectra with bond alternation (366), and Kuhn, Huber & Bar (161) have computed them by a modified free-electron method. The new calculations of Ooshika (367) indicate that bond alternation may begin in symmetrical cyanines with as few as 10 carbon atoms; Labhart's calculations (368) had indicated a lower limit near 30. Abe (369) has given a theory of solvent effects on these spectra. Goodwin (370) has calculated bond lengths in diphenyldiacetylene and a complex polyyne chain. Bond lengths in cumulenes have been inferred from infrared spectra (371). The

optical anisotropy of polyphenyls has been examined (372).

Krauch (373) has demonstrated by spectral comparisons that the polyacetylenes, like polyenes, do not approach the equal-bond-length (cumulene) structure with increasing chain length. It has been predicted that polyenes might form donor-polyene-acceptor (trimolecular) complexes in which the electron displacement would equalize the bond lengths and shift the spectra by thousands of Angstroms, with possibly important consequences for visual pigments and photosynthesis [Kropf & Hubbard (374); Platt (375)]. The spectra and structure of the visual pigments are those of a Schiff base complex of 11-*cis*-retinene with opsin [Hubbard (376)]. Related photochemical studies have been made on polyenes [Oster (377)]. The spectra of arylbutenes, arylbutadienes, and arylbutenynes have been measured (378). Miller & Hannan (379) have shown that the first (forbidden) transitions of dicyanoacetylene are like those of the isoelectronic polyyne, but 5000 $cm^{-1}$ higher; the analysis helps confirm some of the polyyne ($\pi\pi$) assignments [Platt (174); Beer (380); Serre (381)]. Jaffé & co-workers (382, 383) have made a definitive analysis and assignment of the first five n-$\pi$ and $\pi$-$\pi$ singlet-singlet transitions of azobenzenes and their conjugate acids. Their photoisomerization and spectra, and those of aryl azines have been studied [Fischer & Frei (384)]; also their hydrogen-bonding effects (385).

*Nonalternating systems.*—McGlynn & Simpson (386) have applied the Pariser-Parr method to chain amidinium ions. Grammaticakis (387) has studied the spectra of symmetric diarylformamidines. Simpson & co-workers (533) made assignments of the transitions in the pyridocyanines. McRae (388) has made an extensive experimental and theoretical analysis of merocyanine spectra, confirming quantitatively the prediction of spectral sharpening (174) near the isoenergetic (equal-bond-length) point in changing solvents. The electronic structure of these dyes has also been studied by infrared spectra (389). The fluorescein spectra and their prototrophic forms have been studied [Zanker & Peter (390)]; the spectra of derivatives [Emmart (391)]; and the absorption and fluorescence of concentrated (dimer) solutions of similar dyes [Förster & König (392)]. Bonding in urea has been examined (393); and the triarylmethane spectra [redox potentials (394); thioaromatics (395)].

Other spectral studies on dyes include: the effect of adsorbent (396); concentration effects (397); polarization phenomena in amyloid complexes (398); photochemical stability in the solid state (399); the interaction of direct *azo*-dyes (400); and the substantivity to cotton of Congo red and chrysophenine G (401). A thin-cell device for studying concentration effects in strong dyes and biological stains has been described (402).

## Porphyrins and Chlorophylls

A major advance in the interpretation of the porphyrin spectra has been made by Gouterman (403), who showed that a single perturbation parameter (electronegativity) determines the wavelength and intensity changes of both the $^1Q$-$^1A$ (red bands) and the $^1B$-$^1A$ ("Soret band") transitions in

the $D_{4h}$ metal porphyrins; and that a similar approach predicts the free-base spectra much more accurately than the best earlier treatments (174, 404). Ooshika & co-workers have treated phthalocyanine theoretically (405); see also (267). Weigl (406) used polarized fluorescence and confirmed some of the theoretical predictions. Nyholm (407) discussed metal porphyrin spectra and bond types. Improved spectra of pure porphin were given by Rimington & co-workers (408); and of metal tetraphenylporphins by Thomas & Martell (409). The relations between the magnetic, optical, and chemical characteristics of hemoglobins (410) and haemin-haem systems (411) have been discussed. The binding in hemoglobin azide has been examined by electron resonance (412) and explained theoretically (413).

In chlorophyll, the Mg—N bond character has been discussed (414). The spectra of bacteriochlorophyll have been measured [Goedheer (415)]; and of chlorophyll crystals [Jacob *et al.* (416)]; and of adsorbed chlorophylls, with a new technique [Smith, Shibata & Hart (417)]. The spectral and energy-transfer relationships in photosynthesis between chlorophyll and cartenoids have been discussed by several authors (375, 418 to 423). Tollin, Sogo & Calvin (424) have discussed their solid-state electron-transfer and energy-transfer model of photosynthesis; and Franck (425) has given further justification of his two-quantum hypothesis.

### Biological Compounds

Pullman & Pullman and Pullman & Tarrago have discussed the electronic structure of purines (426), their basicities (307a), and donor-acceptor properties (427a); carcinogenic amines (427); and folic acid fragments (428). Charge distributions and energies in peptides and their complexes have been calculated (429); and in proteins (430). The relation of electron mobility to carcinogenesis has been discussed (431).

Further spectra of peptides have been measured (432, 433, 434), tyrosine (435), and proteins at low temperatures (436).

The spectra of brominated purine and pyrimidine bases have been measured (437); of uracils (438, 439); of uridylic acids (440); and of tobacco mosaic virus nucleic acids (441). The fluorescence of ternary nucleotide complexes has been examined (442); and the spectral changes (443) and photochemistry (443a) of nucleic acids after ultraviolet irradiation, and after $\gamma$-irradiation (444).

The spectra of various corticosteroids have been examined in acids (445, 446) and their fluorescence (447); and those of other steroids as functions of conformation (448); and in protein complexes (449). Also Vitamin-D homologues (450); the conessine alkaloids (451); agelin (452); and lysozyme, with changes of pH (453). The spectrophotometry of intact biological materials has been discussed (454, 455); and the following of reaction kinetics (456).

### Ions and Radicals

Longuet-Higgins & McEwen (457) computed the states of the conjugated $C_nH_n$ cyclics ($n = 3$ to 8) with 2, 6, and 10 pi-electrons (closed shells).

Morita (458) has computed the alkylbenzene positive ions; and Murrell (459) the spectra of triarylmethyl radicals. Porter & Strachan (460) have confirmed the two transitions in the spectrum of benzyl (7 pi-electrons), at 4530 A, and 3050 A as found earlier by Schüler and Michel, and have assigned them to the theoretically predicted minus (weak) and plus (strong) combinations of first-order-degenerate one-electron jumps. Mass-spectra studies include further work by Rylander & Meyerson (461) on the configurations of organic ions in the gas phase; and by Inghram & co-workers (462) on photoionization products. McGlynn examined resonance and p*K*a values in polymethinium salts (462a).

Among the ultraviolet spectra studied were the nitrosonium ion (463); the NCO radical (464); a diphenylnitrogenoxide radical (465); the interesting triphenylcyclopropenyl cation (142, 465a); and the solids condensed at low temperatures from electric discharges [Bass & Broida (466); Robinson & McCarty (467)]. Heilbronner & co-workers (468) continued their studies on the benzotropylium series. Hoijtink & co-workers (469, 470), Weijland (471), and van der Meij (472) published an important series of papers on spectra of aromatic positive and negative ions. Arylmethyl cations were studied by Deno & Goodman (473). Dallinga & co-workers studied H-D exchange of aromatics (474) and spectra of their carbonium ions in HF (475) [See also (251).] The agreement with theory is good (476). Aromatics give spectra of simple protonated species in pure HF, but paramagnetic species in $H_2SO_4$, because of photo-oxidation products [Mackor & co-workers (477); MacLean & van der Waals (478); Kon & Blois (479)]. Wassermann (480) studied spectral shifts with proton transfer to polyenealdehydes. The red spectrum of styrene with metallic sodium is attributed to the anion (481, 482). The blue and green colors of carotene with Lewis acids and bases have been reviewed by Körösy (483) [see also (374, 375)].

## SPECIAL SUBJECTS

*Optical rotation.*—The definitive paper of Moffitt, Fitts & Kirkwood (26) clears up the earlier differences between these authors on optical rotation theory, and makes the evidence on the screw sense of polypeptides more equivocal than had been supposed; the validity of the early Kirkwood equations was substantiated, but the Born-von-Kármán boundary conditions were shown to lead to serious errors. Moffitt & Moscowitz (32) showed that peak optical activity should lie to the red of an absorption peak; they applied this to camphor, and predicted the activity of the aromatic hexahelicene from its spectrum (484). On the empirical side, the equations were used in studying helical synthetic polypeptides (484a, 484b); the rotatory dispersion of protein and deoxyribonucleic acid has been discussed (485); and rotation in relation to denaturation (486); some glucosides have been treated (487); and the relation of rotation to spectra studied in various aryl camphors (488, 489) [and see (209)].

*Photochromism.*—The personal debate on photochromism continues be-

tween Kortüm (490) and Hirshberg & Fischer (491). Gutowsky & co-workers (492) could find no electron spin resonance in the colored forms of several photochromic solids (except for an oxygen effect), and Hirshberg & Weissman (493) found none in bianthrone and spiropyrans. But the colored modification of bianthrone may still be a biradical (494); the common feature of the colored forms, biradical or not, may be a chemical rearrangement of bonds, as in the spiropyrans. Reversible colored modifications have now been produced by electron bombardment (495). A transition characteristic of the spiropyranic structure has been found (496).

*Steric effects.*—[See (254, 255, 256, 356).] The angle of twist in various diaryl and triaryl compounds has been predicted theoretically (497). The spectra of hindered biphenyls have been studied by Marcus, Lauer & Arnold (498); and of hindered diarylethers (499). Forbes & co-workers have discussed buttressing effects (500), substituted biphenyls (501), and general steric bathochromic displacements (502); but Heilbronner has criticized the latter paper (503).

*Hydrogen bonding.*—On hydrogen bonds, the theoretical papers include a discussion of force constants (504); an exchange-force model (505); a computation of electronic polarization energies [Fischer-Hjalmars & Grahn (506)]; and a discussion of bonding in amine hydrohalides [Chenon & Sandorfy (507)]. From mass spectra comes evidence on the proton affinity of saturated hydrocarbons [Frankevich & Tal'roze (508)] and on the structure of the intermediate in the reaction of $CH_4^+$ with $CH_4$ to give $CH_5^+$ [Wagner, Wadsworth & Stevenson (509)]. Neutron diffraction shows the H-bonds in potassium hydrogen maleate to be short, strong, and symmetrical (510).

The relation of hydrogen bonds to spectra (511, 512), and their role in dyeing (513) has been discussed. Nagakura & Gouterman (514) have shown spectroscopically that the hydrogen bonds between naphthols and various proton acceptors probably depend on the ease of electronic charge-transfer. The association of oximes has been examined (515). Intramolecular hydrogen bonding has been studied in many molecules: o-nitroanilines (516, 517); nitrophenols (518); hydroxyquinolines [Badger & Moritz (519)]; and aminoanthraquinones and hydroxyanthraquinones of diverse chromatographic properties (520). Intramolecular hydrogen bonding to pi-electron groups has been discussed (521), specifically in 2-allylphenol (522), and phenethylalcohols (523). Hydrogen bonds in meconic acid (524) and in antipyrine (525) have also been studied.

*Solvent effects.*—[See (227, 369, 388).] Nonpolar solvent effects on spectra were treated theoretically by Longuet-Higgins & Pople (526), and dielectric effects by Brown & Coulson (527); a new measure of solvent polarity was proposed by Kosower (528); and a study has been made of micellar environment effects in solubilization (529). Solvent effects on benzene spectra ($\pi$-$\sigma$ versus $\pi$-$\pi$ interactions) were studied [Robertson, Robinson & Babb (530); [and see (226, 227)]; effects on other aromatics [Roe (531)]; and on naphthacene in absorption and fluorescence (532).

## Triplet States and Luminescence

*Major new results.*—The study of luminescence continued to be full of surprises. On the theoretical side, following a treatment by Simpson & coworkers (533) for dimers, McRae & Kasha (534) showed that for an aggregate, the lowest fluorescent or phosphorescent transition from the first band of excited states may be more allowed or much more forbidden (depending on molecular orientation) than in the isolated molecule. This result is relevant to concentration quenching and concentration enhancement of luminescence.

A major experimental achievement was the discovery by Hutchison & Mangum (535) of the long-looked-for paramagnetic resonance absorption in the phosphorescent state—of naphthalene in solid solution in durene—thus proving unambiguously at last that this state is indeed a triplet. The zero-field splitting of the triplet is 0.1 $cm.^{-1}$, mostly due to spin-spin interaction (not spin-orbit!), according to the interpretation of Moffitt & Gouterman (31) [which differs from that of Hameka (536)]. Weissman (537) has discussed the reasons for the difficulty of detecting this triplet in fluid media.

Evans (538) showed that singlet-triplet absorption intensities of many polycyclics depend on the oxygen pressure [perhaps with oxygen-aromatic complexes being formed (539)], and that in deoxygenated benzene, for example, the Sklar absorption bands at 3400 A disappear. Craig, Hollas & King (540) seem to have proved this result dramatically by showing that with vacuum-sublimed benzene, there is no detectable absorption at this wavelength in a 22-meter path of liquid!—indicating that the "natural" oscillator strength of this transition is less than $10^{-11}$ and the lifetime is at least 300 sec. This agrees with the recent calculations of Hameka & Oosterhoff (541) but, if confirmed, will upset all previous experimental and theoretical intensity and lifetime studies on the phosphorescence of aromatics. Also the early Shull-McClure vibration-structure inferences about the symmetry of the triplet states are invalid if the observed spectra are simply those of oxygen complexes.

Kanda & Sponer (542) showed that the phosphorescence spectra of solid toluene are different at 4°K. and at 77°K., probably because of energy transfer at the higher temperature to traces of benzaldehyde produced photochemically from dissolved oxygen.

Delayed singlet-singlet emission ($10^{-3}$ sec.) from aromatic crystals has been so puzzling that it has been held back from publication for years, but it has now been described by Sponer, Kanda & Blackwell (543), and Blake & McClure (544). These authors suggest that the solid-state mechanism that traps the energy for this long time is connected with conduction bands involved in photoconductivity. However, this might also be an illustration of the McRae-Kasha selection rules (534, 545); as might the remarkable delayed fluorescence of aromatics in the vapor phase found by Williams (546) and attributed to dimerization in the excited state. Kasper (547) studied dimerization effects in pyrenes [also see (392)]. Delayed phosphorescence in aromatic carbonyls has been ascribed to chelation (548).

Bäckström & Sandros (549) have shown that the quenching of luminescence from the biacetyl triplet in solution (at least by nonaromatic quenchers) is probably due to the chemical ability of the ($n\pi$) triplet state to abstract an H-atom from a colliding molecule. This is an old suggestion of Plotnikow, revived recently on theoretical grounds (550) to account for some flash-photochemical results on the quinones. Evidently there may be major differences in the photochemistry of a molecule, depending on whether such $n\pi$ triplets are lowest, or $\pi\pi$ triplets are lowest; such an effect would deserve careful study, since in favorable cases the sequence of triplets can be rearranged simply by methyl substitution or by a change of solvent.

*General.*—[See (54, 55).] Furst, Kallmann & Brown (551) have summarized their measurements of fluorescence efficiencies, and oxygen and substituent effects, on 334 organic compounds. Weber & Teale (552) studied compounds whose fluorescent quantum yield is independent of exciting wavelength. Ferguson (553) studied the wavelength-dependence for azulene and several anthracene derivatives. The triplet state in fluid media has been discussed [Porter & Windsor (554); (537)]; and the effect of structure on transition probabilities to triplets (555). The Kasha effect—which is the enhancement of singlet-triplet transitions by heavy-atom or paramagnetic solvents, perhaps through complexes with the solute—has been studied as a function of pressure by Robertson & Reynolds (556); this effect in adsorbed dye molecules has been studied by Clementi & Kasha (557).

Fluorescence polarization techniques have been devised by Ketskeméty & co-workers (558), and the effects of secondary fluorescence have been examined (559).

As for quenching, the theory of diffusion-controlled reactions has been applied by Weller (560); vibrational-energy transfer has been investigated in excited iodine by Arnot & McDowell (561); and in complex molecules by Stevens (562); concentration quenching in fluorescent acenes by Dammers-de-Klerk (563); and cross-quenching by Furst & Kallmann (564). Mataga & Tsuno (565) have studied the effects of solvents on fluorescence, hydrogen-bond quenching, and acid-base relations in pi-electron quenching interactions.

Inorganic luminescent systems activated by organic compounds have been studied (566). The fluorescence spectra and lifetimes of various crystalline molecular complexes have been examined (567). Chemiluminescence has been studied, from dyes (568), and from luminol in the presence of various ions (569, 570).

*Individual molecules.*—Carbonyls and carboxyls: [See (358)]. Hodges, Henderson & Coon (571) have identified the 4-band progression of the 3960 A absorption of $H_2CO$ ($^3A_2$-$^1A_1$ or $^3U$-$^1A$) as the inversion motion of the nonplanar excited state. The spin-orbit coupling in this triplet was calculated by Sidman (14). The analogous transition in acetaldehyde has been studied by Ford (572). The phosphorescence of acetic acid has been studied (573), and viscosity effects on the luminescence of biacetyl (574).

Aromatics: The Schüler emission spectra (glow discharge) of benzenes

have been described further (575). The following have been studied: the luminescence of benzene and deuterobenzene at 20°K. (576); the lowest states of hexamethylbenzene crystals [Wolf (577)]; the emission of toluene (578); the fluorotoluenes (579); the fluorescence of aromatics in solutions [Dammers-de-Klerk (580)]; the triplet state of anthracene in solutions [Livingston & Tanner (581)]; the fluorescence of anthracene and pyrene crystals (269); the absorption and fluorescence of anthracene-phenanthrene mixed crystals as a function of concentration (7); the polarization of fluorescence of stilbene crystals (582) and anthracene crystals (583); the polarization of phosphorescence of phenanthrene [Williams (584)]; the fluorescence of naphthacene solutions (532); and the low-temperature phosphorescence of 3,4-benzpyrene (585). The absence of fluorescence from higher singlets in naphthalene and anthracene vapors shows the efficiency of intramolecular radiationless transitions (586).

Heckman (587) studied the low-temperature phosphorescence ($\pi$-$\pi$) from many 2- and 3-ring cyclics with saturated hetero atoms (1-ring systems had no emission) and showed the lifetimes decrease with increasing Z in the McClure fashion. Freed & Salmre (588) also studied the indoles.

In N-heterocyclics, Clementi & Kasha (589) have made a new computation on the debated question of the increase of spin-orbital interaction in $n\pi$ states. Sidman (12, 13) identified the perturbing state and accounted for the intensity of the $^3B_{2u}$-$^1A_{1g}$ transition in pyrazine, as measured and assigned by Goodman & Kasha (590). The mechanism of quenching in quinolines was examined (311). Bowen & Sahu (591) studied the fluorescence of acridine and acridone.

The fluorescence of thioindigo dyes was studied by Rogers, Margerum & Wyman (592). The spectral changes in photoexcited rhodopsin (triplet-triplet transitions?) were studied by Wulff, *et al.* (593). The luminescence and photoreduction of triphenylmethane dyes as a function of viscosity have been probed (594).

In chlorophylls, the triplet-triplet spectra and triplet decay kinetics were measured by Linschitz & Sarkanen (595) and Livingston & Fujimori (596). Brody (597) has found a new fluorescence in aggregates. Tollin, Fujimori & Calvin have examined the action and emission spectra of green plant materials (598) and the delayed luminescence (reversal of photosynthesis?) (599).

In proteins, Szent-Györgyi & co-workers (600) have continued their emphasis on the biological importance of low triplet states and energy transfer, although Reid (54) has criticized some of the earlier conclusions. The luminescence of tryptophan was examined (601).

Fluorescence studies on other biologicals include steroids in sulfuric acid (602), a morin compound (603), vegetable drugs (604), and epinephrines (605).

*Chemistry of excited states.*—[See (549).] From the Stuttgart group comes the ingenious spectroscopic determination by Lippert (606) of dipole moments in the excited states of various aromatics and merocyanines, and the

measurement by Weller (607) of the p$K_a$ of excited acridine. Kokubun (608) and Baliah & Rangarajan (609) have discussed proton acquisition in the excited state; and Itoh (610) has related base strengths to dissociations in excited naphthalenes. Yamazaki & Shida (611) studied collisional deactivation of excited cyclo-octatetraene.

*Energy transfer.*—Wolf (612) demonstrated that energy-transfer in sensitized fluorescence was not due to simple absorption. Weinreb (613) confirmed this, using a clever technique to distinguish between radiative transfer (simple absorption) and nonradiative transfer (Franck resonance). Birks (614), disagreeing with this conclusion, pointed out a possible source of error, but seems to have been refuted (615). Knau (616) has discussed energy transfer in fluorescent solutions; McClure (617) in double molecules and crystals; McGlynn & Boggus (618) in trinitrobenzene-aromatic complexes; Birks & Cameron (619) in terphenyl-toluene solutions; Crosby & Kasha (620) in ytterbium organic chelates; and Weber (621) in phosphopyridine nucleotides. Teale (423) described energy-transfer from carotenoids to chlorophyll *in vitro;* and the possible transfer in the reverse direction, to carotene-donor-acceptor complexes, has been discussed (375, 418, 419 to 422).

*Photoconductivity.*—Most observed photoconductivity of pure organic compounds is a surface effect, but bulk conduction in anthracene has been reported (622, 623). The valid evidence on this effect is not easy to interpret [Garrett (624)]: for example, the energy gaps determined from the temperature dependence of dark conductivity do not fit the spectral gaps or the photoconductivity threshold; Ohm's law is violated already in weak fields; the dark conductivities are peculiarly small, $10^{-7}$ to $10^{-24}$ ohm$^{-1}$ cm.$^{-1}$ (but appear not to be due to polarization or electrolysis); the front-wall photocell experiment (625) and the sign of the Seebeck coefficient (626) indicate positive carriers. Another survey has been given by Felmayer & Wolf (627). Lyons (628) has discussed the role of ionized states; Rosenberg (629), the role of triplet states [and photoconductivity in the visual process (630)]. Schneider & co-workers (631, 632) related the bulk photoconductivity to spectra in aromatics and showed the effects of melting, of imperfections, and the effect of neutron bombardment (633). Weigl (634) examined tetraphenylporphines; and Suhrmann & Matejec (635) examined soluble organic complexes. Kearns & Calvin (636) have discovered photovoltaic effects and photoconductivity in laminated organic systems (phthalocyanine coated with phenylenediamine), effects possibly similar to those in chloroplasts (424) or in the retina.

### Charge-Transfer Molecular Complexes and Spectra

*Changes in ideas about complexes.*—[See (61, 62).] It is not generally appreciated how many of the original ideas about molecular complexes and their spectra have had to undergo major modifications recently. Orgel & Mulliken (637) showed that even with zero binding energy in some or all geometrical configurations between the two molecules involved, there may

be intense "contact charge-transfer spectra" (638) which will cause large overestimates (approaching infinity) in the extinction coefficients as determined by the Benesi-Hildebrand method of analysis. [Singlet-triplet enhancement by the Kasha effect would appear as such a "contact spectrum" and might make a sizable contribution to the supposed charge-transfer spectra (639), especially in the heavy iodine complexes.] Scott (640) has also pointed out the large possible errors in apparent equilibrium constants and extinction coefficients; and Ardon (641) has discussed the interference of hydrolysis. The work of Smith (642) and Foster (643) on very strong donor-acceptor (but closed-shell) complexes seems to prove within experimental error the earlier empirical suggestion [(639); see also (643)] that the charge-transfer excitation energy is equal to $I_D$-$F_A$, that is, to the ionization potential of the donor minus a constant characteristic of the acceptor, a constant which is more independent of the strength of binding than might be expected theoretically.

The increasingly definite evidence on the geometrical configuration of complexes seems to be contradicting the early charge-transfer predictions. Ferguson (644) showed that in the complexes of iodine with various benzenes, the benzene frequencies that are enhanced in the infrared are those appropriate to a configuration with the iodine molecule lying on the sixfold axis instead of being parallel to the benzene plane. Likewise, Person, Erickson & Buckles (645) found the $Br_2$ frequency appearing in the infrared in bromine-benzene complexes, suggesting that the two Br atoms are not symmetrically located. And Hassel & Strømme (646), using x-rays, found the bromine molecule on the common sixfold axis of the adjacent benzenes in bromine-benzene crystals; and also found (647, 648) halogen-ether and halogen-pyridine structures disagreeing with the early charge-transfer predictions. However, Ferguson & Matsen (649) pointed out that charge-transfer may change during an otherwise forbidden infrared vibration and make it allowed, so that the infrared evidence against certain configurations loses its force; the meaning of these various results is still being debated (650, 62). Fyfe (651) has also criticized the Mulliken theory of co-ordinate bonds in complexes.

Pi-complexes between organic free radicals (N-ethylphenazyl and Wurster's Blue) have been identified by Hausser & Murrell (652) from the behavior of a long-wavelength absorption band which appears at low temperatures. [An acridine-acridinium-iodide spectrum has also been studied (653).]

*General.*—New discussions related to crystal field theory include those of Hartmann (654, 655) on bonding theory; of Ruch (656) (a charming lecture on symmetry relations); of Kolos (657), on spectra of complex ions; of Kiss (658), on symmetry, types of bonds and light absorption; of Moffitt & coworkers (32a), on spectra of hexafluorides; and of Jørgensen (659), on repulsion integrals derived from spectra. Yatsimirskii (660) has discussed the influence of donor $\pi$-bonds on stability of complexes; and Zvonkova (661) has done crystallochemical studies on donor-acceptor bonds. Kosower & Bauer (662) extended the notion of charge-transfer complexes as inter-

mediates to diphosphopyridine nucleotide reactions. Oosterhoff & coworkers (663) found a weak electron spin resonance in solid complexes of polyphenyls with halogens and other acceptors. Kazakova & Syrkin (664) studied the dielectric polarization of halogen complexes.

*$I_2$ complexes.*—The charge-transfer spectra of iodine with ethyl iodide have been studied by Katzin & McBeth (665); of iodine with ethanol by Amako (666) and deMaine (667); with triethylamine by Nagakura & Tsubomura (668); and with aromatics by Bhattacharya & Basu (669). The spectral similarities have led Abe (670) to propose that in amylose-iodine complexes the amylose forms a helical tube containing the iodines, like the Rundle configuration for the starch-iodine complex; it is not clear how this is to be related to the halogen-ether configurations found by Hassel.

*Metal-organic complexes.*—As for the "sandwich complexes"—that is, ferrocene and its homologues, with a metal ion sandwiched between two aromatic rings (18)—Brown (671) has discussed the need of $4p$ orbitals to describe them. Magnetic studies have now been made (672) on the 5- and 6-membered-ring complexes studied earlier (673, 674). Complexes with 4-membered rings were proposed, at least as reaction intermediates (99). [But see (675).] Now that the larger 7-membered tropylium-ion ring ($C_7H_7^+$), and its spectrum is known (676), the spectrum of an analogous tropylium-molybdenum complex has also been found (677).

Studies on spectra of metal chelates include enzyme-metal-substrate compounds [Orgel (678)]; azoquinolinesulfonic acid complexes (679); papers by Kiss on theory (680) and on acetylacetone complexes (681). The nuclear magnetic results of Holm & Cotton (682) on acetylacetone complexes seem to go against the Calvin-Wilson concept of benzenoid resonance in the chelate rings.

Spectral studies on miscellaneous metal-organic complexes include the ferrous quinaldinate system (683); various 8-hydroxyquinoline metal complexes (684, 685, 686); a hydroxyazobenzene system (687); an antipyrinylmethane-cobalt system (688); and some cuprous halide complexes with organics (689); and ferric complexes (690).

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# VIBRATION-ROTATION SPECTROSCOPY[1]

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The past several reviewers of this section have commented on the almost overwhelming volume of contributions to this subject, as there undoubtedly are to many others. It is interesting that at the time of this writing we are informed (1) of a report of the President's Science Advisory Committee in which it is stated that " . . . the rapid rate of scientific progress has multiplied the volume of information to a point where it can no longer be published and handled within the framework of existing methods." The Committee also is reported to have suggested that science apply its own genius to solve the information problem with modern machinery. Assuming the prophetic nature of the Committee, this reviewer is inclined to be envious of those of the future, "robots" though they may be.

The number of titles per year relating to this topic is now in excess of five hundred. We are thankful therefore for the Editor's preference for a critical rather than encyclopedic review. Three years ago the reviewers of this department (2) pointed out that 40 per cent of all pertinent contributions appeared in the *Journal of Chemical Physics*. Last year's reviewers (3) observed the appearance of one new journal and a change of emphasis in another which may have relieved some of the burden on the *Journal of Chemical Physics*. This year has seen the launching of another new journal, *Molecular Physics*, whose pages offer one more stage for molecular spectroscopists. By virtue of all this relief to the *Journal of Chemical Physics*, that periodical now appears to contain less than 10 per cent of the offerings in this field.

Compared to the other divisions of physical chemistry, molecular spectroscopy is far from hoary. Nonetheless, the field witnesses currently few new developments in its principles and new concepts, relative to its status 15 to 20 years ago. It would be difficult to refute the observation that the majority of papers in this field in the past few years have consisted of the applications of principles and methods whose origins are only occasionally current. This observation is by no means intended to be doleful. In each application, there is some new insight or perception so as to make the contribution worthy of attention. The insight that a certain principle, in a particular instance, may be applied is as creative as the invention of the principle.

Witness the progress of our knowledge of stereochemistry. We are especially fortunate this year in being able to consider this question in fair retrospect, due to the recent publication of a handbook (4) on interatomic

[1] The survey of the literature was completed in December, 1958.

distances, bringing up to date the tables on molecular structure published 10 years ago by Allen & Sutton (5). From the point of view of physical chemistry, there is little doubt that increasingly accurate determinations of bond distances and angles will eventually be of great service, such as in valence theory. However, it is well to bear in mind our obligation to chemistry as a whole and inquire to what extent the evaluation of a molecular parameter to the precision of one part in $10^5$ or $10^6$ is appreciated.

The central fact of chemistry is that $A$ reacts with $B$; the greatest utility of structural determinations to chemistry has been in furnishing conceptual information to the working chemist—the reaction kineticist or the theoretical organic chemist. Such information is, for the most part, contained in what shall be called here the "gross structure" of the molecule. Organic chemists for many years were guided in their thinking by strictly two dimensional representations of molecules. Indeed, very brilliant and often successful researches have been stimulated by inspection of such models. Today the "stick-and-ball" models have virtually replaced the older representations in "flatland." These vary from inexpensive student kits to scale models capable of demonstrating even the finest structural details of the $\alpha$-helix. All of these serve to guide, stimulate, and inspire even physical chemists! The requirement of precise information (e.g., better than 0.1 A) is, of course, far from negligible; however, in the absence of more precise theories of valence, of intermolecular interaction, of "nonbonded" interatomic interaction within molecules, the qualitative conceptual contribution to organic chemistry will remain the greatest dividend of molecular spectroscopy.[2] It may even be argued that the new qualitative concept is always the commodity of greatest value—rather than its precise, quantitative determination; the notion of a chemical bond has stimulated far more new chemistry than all the precise bond distance determinations.

We are in need of new concepts. In this connection, to quote Ingold from his Chemical Society Presidential address of 1954 (6),

" . . . most molecules spend the whole of their lives in one state, . . . which we call the ground, or normal, state. However, all other states, the so-called excited states, simply by their potential existence, and even if the molecule will never occupy any of them, determine important properties of the normal state, particularly those properties which are of main importance for reactions."

"Now that . . . investigators have discovered so much of what there is to know about shapes and sizes . . . of most of the simpler typical molecules in their normal states, they should be attracted by the wealth waiting to be won in new knowledge about the morphological . . . properties of excited molecules. . . . "

It has been the pleasure of this reviewer to observe in the past year the beginning of such endeavors. Particular emphasis to this subject therefore will be given.

[2] This statement may be true also for inorganic chemistry, if the number of contributions is suitably normalized, e.g., by the ratio of organic to inorganic molecules (100:1?).

The problem is not an easy one. The lifetimes of excited molecules are rarely long; they are curtailed by both radiative and collisional processes. Existing experimental methods, suitable for the ground state, often have response times many times greater than the natural lifetimes of the excited molecues. The recourses are therefore to shorten the response times of our instruments and make conditions suitable for "unnatural" lifetimes. Advances in both techniques have been reported in the past year.

Before reporting these, there is one more statement of emphasis to be made. It was observed above that there is some question about the need for exceedingly precise interatomic distances in the absence of better theories of intermolecular interaction and of "nonbonded" interatomic interaction. An example would be the present-day status of the origin of barriers to internal rotation (7). Here again the theorist needs, not numbers, but a few well-planned experiments to sense the kinds of parameters of importance in these interactions.

We shall give primary emphasis therefore to these two subjects, Excited Molecules and Interacting Systems.

## Excited Molecules

While Ingold's advice to young spectroscopists is in terms of electronically excited states, these are by no means all of the states concerning which we have sparse information. There is an abundance of ignorance, for example, of the mechanics of molecules in high-vibrational excited states. Indeed, the mode of relaxation of vibrationally "hot" polyatomic molecules is still one of great mystery. Furthermore, the study of electronically hot molecules by conventional methods is often impossible.[3]

The most direct method of study of an electronic upper state is by absorption spectrometry of the ground state. Here, the spectroscopic parameters of the upper state are directly involved and there is no dependence upon the lifetime of the upper state. Most noteworthy is Ingold & King's study of acetylene (8). If the ground state is itself short-lived, as is true for those species often produced photolytically, the method of flash photolysis may be used, as exemplified by Ramsay's (9) work on $NH_2$. As the molecules investigated by these methods become more polyatomic, as is well known from the history of ground state investigations, these spectra may become hopelessly complicated. In order to obtain the desired structural information, it is necessary to disentangle from the spectrum the vibrational and rotational parameters. Unless the molecule has an abundance of symmetry (such as $D_{6h}$), it may be impossible to unravel these details. Of considerable value for background information in this subject are the published papers of a recent symposium on structure and reactivity of electronically excited species (10) and a recent review by Reid (11).

For reasons mentioned above there has been some utilization of methods other than ultraviolet and visible absorption spectroscopy. Notable among

[3] Even by nonconventional methods, these studies are still sparse. For this reason we shall include the study of *any* excited state in this chapter.

these have been the use of electron spin resonances, particularly as used by Ingram (12), Weissmann (13), and Whiffin (14). A monograph by Ingram (15) will undoubtedly be useful for years as the standard reference work on this subject. Probably the most noteworthy achievement in this field for several years occurred in this past year in the observation by Hutchison & Mangum (16) of a spin resonance by the naphthalene molecule in its triplet state.

Unhappily, the elucidation of molecular parameters from electron spin resonance data is a very indirect method at best. We are driven therefore to the more classical techniques of vibration spectroscopy.

There have been numerous attempts to derive upper state data from emission spectroscopy in the infrared, the most recent of which is that reported by Cashion & Polanyi (17). The problem of self-absorption, however, appears to be insuperable. This year has witnessed a success in absorption spectroscopy which foretells perhaps a significant change in the entire time scale of infrared techniques. Tanner & King (18) have followed the flash photolysis of hydrazine by rapid-scan infrared absorption spectroscopy, using a lead telluride photoconductive detector with a 10 $\mu$sec. time constant. The evidence for an unstable species with a half-life of 0.7 msec. is good. The authors make reasonable the identification of this species as the $NH_2$ radical. Using the valence angle of 103° found by Ramsay (19) and the assignments, $\nu_1 = 3200$ cm.$^{-1}$ and $\nu_3 = 3280$ cm.$^{-1}$, the stretching and bending force constants are found to be 5.74 and 0.31 md/A, respectively. By a simple valence force field, $\nu_2$ is predicted from these to be 1060 cm.$^{-1}$. While these force constants are similar to those of other $NH_2$ molecules and the value of $\nu_2$ may also be reasonable, the identification of the species must certainly be viewed as provisional until either $\nu_2$ is directly observed or $\nu_1$ and $\nu_3$ are checked by deuterium substitution. If confirmation is obtained, this is to be sure not an excited molecule in pristine form; but it does qualify as a metastable molecule of principal importance in chemical reactions.

The success of Tanner & King has depended on the fact that the lifetime of $NH_2$, while short, is apparently greater than ten $\mu$sec. Now, electronically excited species, in their singlet states derived by allowed radiation processes from singlet normal states, surely will not have the distinction of such longevity. On the other hand, nature has apparently blessed the spectroscopists with not a small number of molecules which can be coaxed into their triplet states by radiationless processes. The infamous lifetimes of such molecules makes them eligible for such study.

Another important new technique is that reported by Hurzeler, Inghram & Morrison (18a), in which a vacuum ultraviolet monochromator was combined with a mass spectrometer. The first derivative of the ion current with respect to the photon energy is shown to demonstrate, in favorable cases, vibrational structure, from which, ultimately, upper state geometries may be won.

The continued exploitation of matrix isolation by Pimentel and his stu-

dents, and others, has indicated that this technique offers as much, if not more, of an opportunity for the study of metastable species as does rapid scanning. Pimentel (20) has recently reviewed the opportunities offered by this technique and the reader is referred to his article.

Pimentel & Baldeschwieler (21, 22) have used matrix isolation to study the kinetics of the *cis-trans* isomerization of nitrous acid. While there remain certain experimental difficulties with the system, the process seems to be a quantum mechanical tunneling, with kinetics that are not inconsistent with the 12 kcal./mole barrier to internal rotation derived from the torsional frequency (23).

Brown & Pimentel (24) have studied the photolysis of nitromethane and methyl nitrite in an argon matrix. They have thereby confirmed the mechanism for the decomposition of nitromethane originally proposed by Hirschlaff & Norrish (25). The activated form of nitromethane which decomposes to the products—formaldehyde and probably the nitroxyl radical—is shown to be methyl nitrite, in its *trans* form. The demonstration that the preferred conformation is *trans* confirms the conclusions of the recent nuclear magnetic resonance experiments of Piette, Ray & Ogg (26). The values of the observed frequencies for DNO are close to those calculated for a molecule with valence angle 102°, although a change to 110° would make all the molecular parameters close to those of hydrazoic acid and would hardly change the calculated frequencies. There seems to be adequate reason in theory for making the proposed change of angle. The molecule is predicted by Walsh (27) to be bent. The value of 102° for the bond angle was obtained from Dalby's (28) flash photolysis work; however, this result depended upon the assumption of the N-H bond length. Brown & Harvey (29) claim confirmation of $\nu_2$ (NO stretch) and $\nu_3$ (HNO bend) from experiments on HNO prepared by the addition reaction between nitric oxide and hydrogen atoms. There is some change in the offing for the frequency of $\nu_1$ (N-H stretch) from that observed by Brown & Pimentel (3300 cm.$^{-1}$). This of course will not affect the calculation of the force constants of importance to $\nu_2$ and $\nu_3$. However, it is important for unique identification of the species. In the study of Brown & Pimentel there are a number of high frequency bands which could be assigned as N-H stretching motions. Similarly in the method used by Brown & Harvey for the preparation of HNO, secondary reactions could give species with several bands in the high frequency region. In order for us to have definite information about such an important intermediate as nitroxyl we shall await with considerable interest the final results of the H+NO reaction carried out in matrix isolation.

The provisional success of this reaction suggests the possibility of many other experiments in which addition reactions and even abstraction reactions will be of use. Most such experiments to date have been based upon dissociation reactions, R-R′ is placed in a matrix and photo-dissociated *in situ*. It is then hoped that the fragments (which are hopefully, R and R′) will be blessed with sufficient kinetic energy to escape one another and hence re-

combination. Then R and R′ may be studied spectroscopically; finally, when the matrix is heated, it is expected that R and R′ will properly diffuse and simply form the ultimate products of the reaction.

To date there is insufficient evidence that these delightful happenings will ensue without complications. Above all, there is considerable evidence of the negative variety that in most such experiments to date, if the fragments (R, R′) are produced, their kinetic energy has not been excessive. They thus remain in the same "cage" and politely recombine.

Milligan (30) has accordingly explored those reactions in which one of the fragments is thermodynamically stable, compared to the starting material, so that the activation energy for the recombination is likely to be great. As examples, isolation of methylene radical, $CH_2$, from the photolysis of both ketene and diazomethane, in matrix isolation, was attempted. In the first case, no evidence for methylene was obtained. This was expected, as apparently (31) the back reaction of $CH_2$ and CO is facile. In the other case, however, good evidence for $CH_2$ is obtained which must now be corroborated by repetition with heavy diazomethane, $CD_2N_2$.

This work represents one of the finest examples of matrix isolation procedure. In particular, even in such a "simple" system as diazomethane, the photolysis in a nitrogen matrix at 20°K. produces an abundance of absorption events. These are all sorted, classified, and distinguished one from another by *qualitative* comparisons with results obtained upon permitting the matrix to "warm up"—to a temperature at which diffusion of the captured species takes place (20). Thus, out of roughly a dozen new bands due to either the primary photolysis act, secondary reactions, or various combinations upon warm-up, two bands ($3005 \pm 10$ cm.$^{-1}$ and $1365 \pm 2$ cm.$^{-1}$ in nitrogen; $3010 \pm 10$ cm.$^{-1}$ and $1355 \pm 2$ in argon) are selected as being reasonable fundamentals of the methylene radical. At the same time quite acceptable assignments of the other bands are made. The frequencies assigned to methylene are by analogy reasonable for a bent $CH_2$ molecule, but the other C-H stretching frequency strangely seems to be missing. The absence will be a problem until, e.g., heavy diazomethane is studied. Until the missing frequency is found, we cannot strictly conclude anything about the geometry of methylene. However, we wish to emphasize that the assignment of the two frequencies at hand is felt to be quite reliable and that this has been accomplished completely by qualitative judgments—rough rates of growth and decay of sets of bands, etc.

Uncertain ground will be encountered in attempts to make these methods more quantitative. These will require judgments of extinction coefficients or at least of the transference of extinction coefficients of various bands of standard molecules from control conditions to the actual matrix under photolysis. Such transference requires a knowledge of the quantitative behavior of absolute absorption intensities upon condensation, both in the solid state and in the inert gas matrices. Such knowledge does not exist. Research into absolute intensities in the liquid state is in its formative stage and will be dis-

cussed below. Until such knowledge is available we must be content with careful qualitative studies, such as that by Milligan.

While matrix isolation continues to offer further delights, it is still in an early stage of its development. Brown & Harvey's (29) experiment represents the first use of a "twin-jet" technique; here the reactants (H and NO) were mixed just before deposition on the low-temperature window. Similar procedures have been used by Bent & Crawford (32) in studying the reactions $NO+O_2$, $NO+O_3$, and $NO_2+O_3$. An abundance of new oxides of nitrogen were found, including the sesquioxide, and at appropriate dilutions, monomeric and dimeric NO and $NO_2$. The number of new oxides is large because of the apparent ease, in the dimerizations, of achieving several permutations of arrangements of the monomers with respect to one another. To the chemist these results are very exciting as they provide excellent demonstrations of geometries of reaction intermediates whose existence has been largely unexpected.

In carrying out these experiments, Bent & Crawford have devised an interesting procedure for adding short bursts of heat to the condensed matrices. To date, heating has been carried out only by removal of refrigerant or the careful regulation of electrical resistance heaters. Bent & Crawford have demonstrated that carbon dioxide, admitted with a third jet, can be used to "blanket" the sample. The molecule is simple enough so that its contribution to the spectrum cannot be mistaken, and the heat of condensation of small amounts can serve to warm the condensate just a little. Thus diffusion and its effects may be studied in gentle bursts rather than all at once.

> As winds come whispering lightly from the West,
> Kissing, not ruffling, the blue deep's serene (33)

Closely related studies to those just mentioned have been those performed under the National Bureau of Standards Free Radicals Research Program. A major portion of these has been concerned with infrared examination of condensates of simple gases, such as $N_2$ and $O_2$, which have been passed through high frequency electric discharges. An excellent example is that of Harvey & Bass (34), in which the products of an oxygen discharge were studied at 4°K. and compared with the spectrum of ozone (also recorded at 4°K.) and with the known absorption of several oxides of nitrogen. As these studies undoubtedly will be discussed by a reviewer in another chapter in this volume, only this representative article is called to the reader's attention.

A difficult question in all matrix-isolation studies is the degree of crystallinity of the deposits. In many instances this question is overlooked; in some studies it is unanswerable and leads to ambiguities of interpretation. The researches on absorption-intensity phenomena in the condensed state, reviewed below, may be helpful in answering this question.

As mentioned previously, the mode of relaxation of vibrationally "hot" polyatomic molecules is still poorly understood. However, the progress in

understanding the process in diatomic molecules is becoming overwhelming. The series by Shuler *et al.* has now been extended to cover the relaxation of systems of anharmonic oscillators (35) and rotating oscillators (36).

A year ago Klemperer & Herschbach (37) presented a novel analysis of the relative line intensities in the molecular beam-electric resonance experiment on LiCl of Marble & Trischka (38). Klemperer & Herschbach proposed that the efficiency of ionization of LiCl molecules on a hot wire detector varied depending on the vibrational state of the LiCl molecules. Herman & Rubin (39) have now found the steady-state population distribution of such molecules over the vibrational states by use of the general method of solution of vibrational relaxation equations developed by Montroll & Shuler (40). In addition they have discovered that the vibrational energy accommodation coefficient on a surface has a simple form, which depends only on the evaporation rate constant (assumed to be independent of vibrational state), a rate constant for changes in vibrational state, the temperature of the surface, and the vibrational energy spacing of the harmonic oscillator being evaporated.

## Interacting Systems

This section will be concerned, firstly, with intermolecular and, secondly, with intramolecular interactions. While the latter forces are admittedly of less importance than those involved in what we call chemical bonding, we must recognize that if we indeed wish precision, we may even have to sacrifice a concept—that of bonds. We must then recall that the quantity we should manipulate is the electron-density function of the molecule, which may have a finite value anywhere in the space of the molecule. Indeed, by not doing this, we have perpetuated the oversimplification that we call the "stick-and-ball" model. Here is another demonstration of a conceptual constraint. However, we shall look for new concepts among, first, intermolecular interactions. We could describe the relationship of this field to chemistry by recognizing its importance at the outset of any chemical reaction, prior to the subsequent atomic rearrangement but when distances of approach are of the magnitude of atomic diameters.

These notions, of course, bring to mind gas imperfection and consequently the continuation of the researches begun several years ago by Welsh (41), Vodar (42), Ketelaar (43), and their associates.

This past year Britton & Crawford (44) have re-examined the theory of collision-induced absorption of hydrogen, improving on the earlier theory of van Kranendonk & Bird (45) and of van Kranendonk (46). The integrated absorption coefficients for the $Q$ branch and several $S$ branches were calculated for room temperature and also for 80°K. The calculation is for a pair of molecules whose wave function is taken to be the product of the vibrational and rotational wave functions of the separate molecules (the latter defined in terms of the intermolecular axis) and the ground electronic state function of the system. The latter is taken to be an antisymmetric linear

combination of determinantal functions of Rosen atomic orbitals (and spin functions) for each of the four electrons of the system. The induced dipole moment of the pair is expanded in a Taylor series, and the matrix elements appropriate to the fundamental band are derived from the first derivatives of the induced moment by expanding in products of spherical harmonics. The coefficients in this expansion are then evaluated by first breaking up the dipole moment into two parts, $\mu_a$ and $\mu_q$. The former results from overlap forces and is calculated by considering the interaction of atom pairs. The dipole moment is explicitly calculated in terms of the coordinates of all particles of the two-hydrogen-molecule system, using the electronic wave function previously described. $\mu_q$ is a result of the interaction of the quadrupole moments of the two molecules and is obtained in two independent ways. The first, which is theoretical, uses the parameters of the Rosen orbitals; the second, which is semiempirical, uses polarizability data and also data concerning the first derivative of the polarizability, determined from the field-induced absorption studies of hydrogen by Crawford & McDonald (47). This parallels the method used by van Kranendonk (46). It is based on the hypothesis that

$$\mu_q = \alpha_2 \dot{E}_1 + \dot{\alpha}_1 E_2$$

where molecule 1 is vibrating and molecule 2 is not, and where $E$ and $\alpha$ are the quadrupole field and polarizability, respectively. Thus, the oscillation of 1 produces a varying field $E_1$ at the locus of molecule 2 and hence a varying dipole moment $\alpha_2 \dot{E}_1$. Likewise, the finite but nonvarying field $E_2$ at the locus of 1 produces, again at 1, a varying dipole moment $\dot{\alpha}_1 E_2$.

The theoretical calculation of $\mu_q$ is begun by a direct computation of the expectation value of the contribution to the dipole moment due to all electrons, using electronic wave functions for a perturbed system, in which the perturbation is the Coulombic interaction between all electrons. The form of the resultant equations for the upper limit of $\mu_q$ suggests a variational calculation which results in a calculation of $\mu_q$, using the Rosen functions again and only the dipole-quadrupole term in the expansion of the Coulombic interaction.

The results of the two procedures for obtaining $\mu_q$ are then examined by adding each to $\mu_a$, and the sums are compared with the experimental data for the integrated absorption coefficients. These have been determined by Welsh & co-workers (48, 49, 50) at room temperature and by Hunt (51) at approximately 80°K. Britton and Crawford find that at 296°K., the theoretical intensity is less than the experimental, while the semiempirical calculation predicts a greater intensity than was observed. For 80°K. the predicted intensity is in each case greater than that observed, which they suggest is due to the fact that the molecular pair distribution function they have used should have been quantal rather than classical.

Van Kranendonk (52) has extended his earlier work on this subject by a somewhat similar procedure to that used by Britton & Crawford. A 6–12

potential was used, as they did, in the pair distribution calculation. However, instead of the explicit calculation of the overlap contribution used by Britton & Crawford, van Kranendonk begins by carrying out a semiempirical calculation of the induced moment. He then assumes that while the long-range induced moment decreases as $R^{-4}$, the short-range overlap moment decays exponentially with the intermolecular separation, $R$. The parameters of this exponential law, measuring the magnitude and the range of the overlap moment, are then evaluated by fitting some of the calculated expansion coefficients (44, 53) to the assumed exponential. The induced moment's contribution to the experimental absorption coefficient is then subtracted from the latter, and the parameter which measures the magnitude of the overlap moment is derived. This is called the "experimental" value of magnitude parameter. The agreement with the calculated magnitude parameter is good, but, as van Kranendonk points out, this is not significant; the fact that the two are of the same order of magnitude, however, makes for confidence in the ($exp$-4) model.

Using this model, van Kranendonk has calculated the absorption coefficient as a function of temperature, fitting the derived curve to the known value at room temperature (50). The result is a linear dependence upon the temperature at least down to 150°K., which is qualitatively and quantitatively in good agreement with the experimental data (50).

Hare & Welsh (54) have now studied pure hydrogen and its mixtures with helium, argon, and nitrogen at pressures up to 5000 atmospheres. They can thus evaluate the part of the absorption coefficient due to collision triples. It is found to be approximately $10^{-3}$ that due to collision pairs.

We have referred above to the determination of the matrix elements of the polarizability by the method of field-induced absorption by Crawford & McDonald (47). The effect was first predicted by Condon (55) in 1932, and a preliminary report of its successful realization appeared in 1953 (56). The first reported attempt to accomplish the effect in liquids was carried out in conjunction with an interesting study of the Kerr effect in the infrared by Charney & Halford (57). It is hoped that the details now furnished in these two studies will encourage further pursuit of this technique.

That this is occurring is indicated by the report that this technique is now being studied in at least one more laboratory. Terhune (58) has studied the same system as that studied by Crawford & McDonald but used a 90 cycle AC field and modulated his detection system at the same frequency. Field-induced absorptions as weak as one part in 50,000 were detected.

The pressure-induced rotational absorption spectrum of hydrogen has been studied both experimentally and theoretically by Colpa & Ketelaar (59, 60) and by Kiss, Gush & Welsh (61). Colpa & Ketelaar's analysis of the mechanism of the effect parallels much of the formalism first introduced by van Kranendonk (46). The contribution of overlap forces was neglected, and only the quadrupole-polarizability interaction was considered. A Lennard-Jones pair distribution function was again employed. The resulting

calculated absorption coefficients, in the case of pure hydrogen, were always smaller than those observed experimentally (59).

The relative success of the van Kranendonk-Britton & Crawford theories of interaction of the electrical distributions of collision partners in accounting for intensities that "should not be there" brings to mind the current difficulties with those that "should." For some years now certain intense spectroscopists, using gases at pressures of not more than a thousand or so psi, have been studying the variation in absorption intensities from one normal mode to another. The problems and inconsistencies found in applying the earliest and simplest model for vibrational intensities (62) have hardly changed in 10 years. The major assumptions and difficulties with this model were summarized in 1955 by Hornig & McKeen (63). The assumptions are as follows: "(*a*) when a bond is stretched by d$r$, a moment $(\partial\mu/\partial r)$d$r$ is produced in the direction of the bond; (*b*) when a bond is bent through an angle d$\theta$, a moment $\mu_0$d$\theta$, where $\mu_0$ is the "effective bond moment," is produced in the plane of the bending and perpendicular to the direction of the bond; and (*c*) when any one bond is bent or stretched, no moments are produced in other bonds."

At the time that Hornig & McKean so explicitly formulated these assumptions, the isotopic invariance rules for intensities due to Crawford (64) had not as yet been well tried, and *ad hoc* physical arguments had to be introduced in order to remove the indeterminacy of the signs of $\mu_0$ and $\partial\mu/\partial r$. Even so, Hornig & McKean concluded from a survey of the data then at hand "that the independent, rigid-bond model of the molecule is on such insecure ground that the results reported in terms of $\partial\mu/\partial r$ and $\mu_0$ may not only be in error but in some cases may be quite meaningless."

Hornig & McKean therefore prescribed that all reports of dipole derivatives be made in terms which did not call upon any internal molecular model, such as the use of $\partial\mu/\partial S$, where $S$ is a symmetry coordinate of the molecule. This prescription has been, in fact, followed by Crawford & his associates (65).

Since 1955, Crawford & his co-workers have completed very careful studies, with all necessary isotopic substitution, of a series of molecules well chosen for testing many features of vibrational band intensities. These have included, in particular, ethane (66), methyl chloride, bromide, and iodide (67, 68) and their per-deutero modifications. Even with an insistence upon following Hornig & McKean's prescription and removal of sign ambiguities, there remain uncertainties. For instance, in the study of ethane (66), the direction of the dipole moment developed in the molecule as a whole for each symmetry coordinate may be indicated. However, this direction may be indicated in a consistent way only for each symmetry species; there is no absolute method of relating these directions from one species to another.

The translation of intensity data into statements of the several $\partial\mu/\partial Q$'s, where the $Q$'s are normal coordinates (now, with isotopic substitution techniques) is usually not open to question. Should there be any mixing of states,

the translation should be done by experts. The validity of the next step, however (the following of Hornig & McKean's prescription), depends upon the particular potential energy function chosen. It may be that the criterion for the precision of the potential function in use to date—the reproduction of the experimental frequencies—is not precise enough for handling intensity data.

This past year some of these difficulties have been given a careful review and consideration by Coulson (69). The assumptions of Hornig & McKean are stated and carefully discussed therein. Coulson considers the possible importance of (*a*) the contribution of lone pairs to the total dipole moment and its change, (*b*) changes in hybridization of bonding and lone pair orbitals, (*c*) orbital following (70), and (*d*) the possible existence of transverse bond moments. Hornig & McKean themselves had some earlier thoughts concerning the first three of these matters (63). The importance of all four, in relation to the bond moment hypothesis, is obvious. However, as it is possible to modify vibrational potential energy functions so as to include these concepts, they even may be of importance at an earlier stage of the theory. Item (*a*) above is interwoven in the difficulties with at least the first two assumptions of Hornig & McKean. The remaining items [(*b*), (*c*), and (*d*)] certainly affect all three assumptions.

To date the few trials of force fields which include orbital following (71, 72, 73) do not reproduce frequencies with the precision of the more general functions Crawford and his co-workers have used. Nevertheless it seems at this point that these intramolecular polarizations must be taken into account. The success of the theories of van Kranendonk, and of Crawford & Britton in intermolecular polarization seems to be an additional encouragement to try new force fields. Intramolecular, nonbonded interactions are explicitly used in Urey-Bradley force fields with fair success in reproducing frequencies (74) and in obtaining vibrational amplitudes (75). It should be interesting to try such fields in absolute intensity studies.

There have been encouraging attempts to elucidate the effects of condensation upon vibrational intensities. Foremost among these this year was Buckingham's (76) careful examination of the problem for diatomic molecules. For the first time, the problem for nonpolar media, where only the transition moments can be sources of intramolecular dipole-dipole fields, has been explicitly stated. This problem recently has been given the attention it deserves by Polo & Wilson (77) and by Person (78), after a lapse of over 20 years since Chako's paper (79) on the subject. Polo & Wilson's article was devoted to pure liquids, while Person has been concerned primarily with liquid solutions.

The matter has also enjoyed discussion by van Kranendonk (53). Van Kranendonk has emphasized that there are two types of induced absorption which contribute to the total enhancement of intensity upon condensation. One of these he refers to as "true" induced absorption and is ascribed to the short-range intermolecular forces of importance in the phenomenon of pres-

sure-induced absorption discussed above. The other type, van Kranendonk calls "apparent" induced absorption and is due to the relatively long range dipole-dipole interactions. It is these, and these alone, which have formed the bases of the treatments of Chako, Polo & Wilson, and Person.

Chako's treatment was based on the Debye or Lorentz electric field equations for a dielectric. Polo and Wilson proceeded to make use of the more reasonable Onsager model, including the reaction field term. The result is the same as Chako's if it is considered that the constancy of a term involving the dipole moment of the molecule permits neglect of this term. This step has never received adequate explanation. Part of the difficulties lie in the explicit substitution $\epsilon = n^2$. As Buckingham (76) has shown, this substitution is valid when the dipole moment used is the oscillatory dipole resulting from the molecular vibrations. If this is implicit in Polo & Wilson's treatment, it would seem that their final equation is valid only for nonpolar, nonrigid molecules; and the term involving the dipole moment then should be as oscillatory as the term containing the elected field.

Buckingham explicitly defines the reaction field as

$$F = g_\epsilon m_\epsilon + g_n \Delta m$$

where $\Delta m$ is the oscillatory dipole and the g's are the reaction field factors $2(\epsilon-1)/(2\epsilon+1)a^3$ and $2(n^2-1)/(2n^2+1)a^3$, respectively. Proceeding from here, Buckingham uses straightforward expansions of the various moments and first- and second-order perturbation theory to obtain solution-to-gas intensity ratios for fundamentals, and first and second overtones of polar and polarizable diatomic molecules. The result requires a knowledge of the molecular shape (spherical, disklike, etc.); the dielectric constant and the index of refraction; the first derivative of the polarizability and its equilibrium value; and the permanent dipole moment of the molecule. However, even with reasonable approximations, including $\epsilon = n^2$, it is difficult to obtain a result for a pure liquid of a similar form to that of Chako, Polo & Wilson, and van Kranendonk (53).

Schatz (80) has compared the absolute intensity of $\nu_3$ of carbon disulfide in the liquid and the gas. The Polo & Wilson relationship predicts a 44 per cent increase in intensity upon condensation. The observed ratio (liquid-to-gas) is 2.06.

In view of these difficulties, we look forward to the continuation of the application of the short-range force theories to liquid phase intensities. We foresee at least one problem. In the study of collision pairs, it may be appropriate to do as Britton and Crawford have done—to evaluate the induced moments for certain special and important relative orientations of the colliding pair of molecules. However, for clusters of molecules in liquids, one would expect that orientation averaging of the intermolecular forces would be appropriate. Herein lies the problem, for if all orientations are considered equally likely, the quadrupole-polarizability interaction term averages to zero. The finite line width of nuclear magnetic resonance transitions in

liquids testifies to the fact that complete orientational averaging is inappropriate. The clustering of groups of molecules in liquids or their tumbling (or both) is, of course, asymmetric. Such asymmetry must persist for periods of time commensurate with the "time" of a nuclear magnetic resonance "experiment" and will thus be certainly effective over many vibrational periods.

We turn now to matters of intensity in the solid state, where orientations are fixed. A year ago, Hornig & Hiebert (81) began to report their study of molecular interaction in mixtures of HCl and DCl in the solid state. By the application of the hypothesis (originally a result of the work of Decius (82, 83, 84)) that such interactions may obey a simple dipole-dipole ($R^{-3}$) law, where the dipoles are the transitory $\partial\mu/\partial Q$'s of individual but interacting members of molecular pairs, triples, etc., one may evaluate with further assumptions the dipole derivatives $\partial\mu/\partial Q$. These assumptions are almost too numerous to state. One must be confident of the crystal geometry, of certain matters of chain statistics, of where the transition moments in the individual molecules are located, and, for polyatomic molecules and nontrivial crystal structures, of the validity of fairly primitive secular equations.

Hornig & Hiebert's study (81, 85) of diatomic molecules is saved of many of these difficulties. However, there seem to be at least two with some remaining uncertainty. By inspection of the most probable HCl lattice, they apparently find that of the four different kinds of first nearest neighbors of a particular molecule, one kind is much closer to that molecule than the other three. This then permits discussion and analysis of their results in terms of what may be viewed as one-dimensional chains. If the dimensionality is greater than this, the chain statistics become very difficult. However, for dipole-dipole interaction, it would seem that the parameter which should be compared is the appropriate trigonometric factor for molecular pairs ($\cos\theta_{ik} - 3\cos\theta_i\cos\theta_k$), divided by the cube of the intermolecular separation. If this is done, rough calculations suggest that the chains in solid HCl are more networklike than one dimensional.

Another difficulty is the locus of the transition moment. Hornig & Hiebert use an intuitive argument for locating this on the protons in HCl. Existing theories for elucidating the symmetry species of the normal vibrations of molecular crystals (86) would seem to suggest that by symmetry the locus of a molecule's transition moment, even in a crystal, would be at the center of mass of the molecule.

The proton positions in the hydrogen halides, are not altogether certain (87). The crystal structure of solid hydrogen fluoride has been more amenable to study; it has had excellent x-ray diffraction examination by Atoji & Lipscomb (87). A similar investigation to that of Hornig & Osberg (88) has been recently completed by Giguere & Zengin (89). Unfortunately, there are not many small polyatomic molecules (aside from diatoms) with determined crystal structures for further examination of the validity of the Decius hypothesis and testing of its assumptions.

Probably the next most suitable is methyl chloride. The crystal structure of this substance has been determined by Burbank (90). This crystal structure was used several years ago by Hexter (91) in an attempt to interpret the spectrum of methyl iodide obtained by Mador & Quinn (92). It was concluded that the two methyl halides were isomorphous.

More recent data on these halides (and on methyl bromide also) has been reported by Dows (93). The spectral resolution used was a substantial improvement over that available to Mador & Quinn. Nevertheless, the study, in some ways happily, posed more questions than it answered. First of all, the improved resolution demonstrated that $\nu_5^{CH_3}$ (e) of methyl iodide is a quartet, and not the expected triplet. Methyl iodide therefore cannot be isomorphous with methyl chloride, and its spectrum should not be interpreted in that light. Secondly, the procedure of Hornig & Osberg (88) for obtaining the angle between the principal axes of the symmetric top molecules sharing unit cells yields different results depending on which parallel band (of $CH_3Cl$) is selected for the test. That the method should fail for the perpendicular bands is not too surprising. Most puzzling, however, was the observation (even in methyl chloride) that the multiplicities due to both site and factor group effects are not even of the same order of magnitude for all normal modes of the same species. Thus the perpendicular bands, which should all be triplets, Dows resolves as follows: $\nu_4$ is a doublet, $\nu_5$ is a triplet, and $\nu_6$ is apparently a singlet, even with a spectral resolution in the vicinity of 1 cm.$^{-1}$

There is no hint in the spectrum of methyl iodide of Mador & Quinn that $\nu_5$ is a quartet. Dows' observation has been confirmed in our laboratory by Milligan & Hexter (94). The quartet consists of two groups of lines, in each of which the low frequency member is the more intense. The separation within groups is approximately 5 cm.$^{-1}$; the separation of the two groups is approximately 25 cm.$^{-1}$. In view of the puzzles noted above, there is no way of deciding from the spectrum itself which of these is due to a site group or to a factor group effect. In our laboratory we (94) have carried out mixed crystal studies of the several methyl halides one with another, and also of methyl iodide with methyl iodide-$d_3$. As a result of these experiments there is no doubt that the 25 cm.$^{-1}$ splitting is due to simple removal of the double degeneracy by the changed site symmetry; the finer splitting in pure methyl iodide is a coupling effect. Observations on the analogous band of pure methyl iodide$-d_3$ (94) demonstrate only a doublet at a spectral resolution of less than 0.6 cm. This change from the situation in methyl iodide (the quartet) can be correlated with the assumption of a monoclinic unit cell, a dipole-dipole coupling of the type proposed by Decius (82, 83, 84) and the well-known dependence of intensity upon isotopic substitution (64). The studies discussed immediately above have been facilitated by the recent commercial availability of diffraction gratings for the infrared. Their use, coupled also with the relatively new technique of matrix isolation and, in general, cryoscopic techniques, offers much for future work in infrared

spectroscopy. As examples, preliminary observations (95, 96) have demonstrated a remarkable fine structure in dilute solutions of water and ammonia in the solid inert gases. Also considerable resolution of $\nu_3$ of methane and silane has been achieved (96, 97, 98). It is anticipated that these observations may be of value in discerning information on restricted rotation in the solid state. Several studies pertinent to this subject have been reported this year by Busing & Morgan (99), Wickersheim (100), Megaw (101), and Hexter (102, 103, 104). Most noteworthy is the report of Vedder (105) on the one dimensional rotation of the ammonium ion in solid solution in KCl, KBr, and KI.

This subject is for the most part in its infancy, for the solution of the wave equation for polyatomic molecules rotating in external crystalline fields has been worked out for only one system (106). Restricted internal rotation in molecules is, of course, an old subject. One might hope that by now we would know enough about its properties and sources for transference to the related problem in the solid state. Unhappily, the theoretical understanding of the barrier to internal rotation has not progressed much in the year since Wilson's (7) conclusion that the source was not to be found in interactions between the bonding orbitals. Pauling (107) has rebounded from this conclusion with a theory which places emphasis on the possible *d* and *f* character of, the C—H bonds in ethane, for example, and to the overlap forces between these. The cost in promotion energy to include *d* and *f* character seems only a little less than that necessary to include *g*, etc., character. It is not indicated why these do not enter into the amended description of C—H bonds. Also, the theory makes no mention of the radial parts of the bond functions, which must play an important role in the calculation of the overlap energy.

E. B. Wilson, Jr., his students, and colleagues have continued in accumulating values for barrier heights in specific molecules. These have been, for the most part, determined from frequency measurements of the fine structure in the microwave spectrum resulting from the interaction of internal and over-all rotation. Thus Lide & Mann (108) have determined the barrier in trimethylamine to be 4400 cal./mole. This is a "one-dimensional" barrier—the forces between different methyl groups is surprisingly small. Swalen & Stoicheff (109) obtained a barrier of 1255 cal./mole in methyl difluorosilane. Pierce (110) found the corresponding quantity in the methyl fluorosilane to be $1559 \pm 30$ cal/mole. In propylene oxide, Herschbach & Swalen (111) obtained the value of 2560 cal./mole. Finally, Lide & Mann (112) have extended the procedures in their study of trimethylamine to isobutane, tertiary butyl fluoride, and trimethyl phosphine. Again the forces between different methyl groups are small; the barriers are, respectively, 3900, 4300, and 2600 cal./mole.

Verdier & Wilson (113) have developed a method of using relative intensity measurements of rotational lines and their torsional satellites for the

determination of barrier heights. They obtain the following for acetaldehyde and ethyl fluoride, respectively: $1103 \pm 60$ and $3310 \pm 210$ cal./mole. These are in good agreement with the values obtained from the frequency splittings calculated by Kilb, Lin & Wilson (114) and by Herschbach (115).

Most of these microwave studies and many others arrive at very precise values of bond lengths and angles. Indeed, there is one report (116) of bond lengths with a precision of $1 \times 10^{-4}$ A. In the sense of our emphasis on "interacting systems," there is hardly space to even cite these, let alone the many other subjects that traditionally form a part of molecular spectroscopy. We cannot leave the subject of bond distances however without calling attention to an empirical relationship, which while it is quite preliminary seems so new and simple as to make it particularly noteworthy. This relationship was reported by Stoicheff & Costain (117) and consists simply of the observation that to considerable precision, the carbon-carbon bond lengths in substituted ethanes and ethylenes are directly proportional to the number of bonds "attached" to the central bond; or to the sum of the exponents $n$ in the symbols $sp^n$ which describe the "ideal" state of hybridization of the two carbon atoms which define a "central" bond.

"The sensations are signs to our consciousness, and it is the task of our intelligence to learn to understand their meaning" (118).

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# THE SOLID STATE[1]

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The quantitative impression gained from scanning the pages of *Physical Review* is that about one-third of current physical research is in the field of the "solid state." This survey is not intended to select the most important papers from such an extensive activity, but to mention recent work of significance related to the author's fields of interest. In particular, little reference will be made to the theory and electronic properties of metals; but attention is again called to two excellent recent reviews of these subjects, by Herman (1) and Lax (2). The lectures at the 1957 Italian summer school, on quantum theory of solids, lattice defects, and semiconductors, provide splendid introductions to these subjects (3). The immense field of semiconductors now has its own abstract journal (4), and it will not be discussed here. Any eccentricities in this review may be ascribed to the fact that the editors have assigned it to a chemist; any merits are due to the generous advice the author received from both chemical and physical confreres. Before the main parts of the review, a few developments of unusual general interest will be briefly mentioned.

The paper *Theory of Superconductivity* by Bardeen, Cooper & Schrieffer (5) gave what appears to be a definitive solution to a major scientific problem. The theory is based on the fact that the interaction between electrons resulting from virtual exchange of phonons is attractive when the energy difference between the electron states involved is less than the phonon energy. When this attraction dominates the repulsion between electrons, a superconducting phase can be formed. The new theory was used by Pines (6) to explain the regularities of occurrence of superconductivity in the periodic system.

It was suggested by Kittel (7) that "spin waves" might be observed in thin films; in a ferromagnet the spins of electrons on adjacent atoms are aligned; if we twist one spin and let it go, a wave will propagate through the spin system. If the spins on the surface of a specimen experience anisotropy interactions different from those in the interior, it should be possible to excite spin waves by a uniform rf field. Such an experiment was successfully done by Seavey & Tannenwald (8), and among other applications the technique should furnish new information on the nature of the surface anisotropies.

The extension of research with ultrasonic waves into the microwave frequency range, up to $2.5 \times 10^9$ c.p.s., has been made in the experiments of

[1] The survey of the literature was completed in November, 1958.

[2] The author thanks the National Science Foundation for the award of a fellowship, during the tenure of which at the University of Paris this review was written.

Baranskii (9) and of Bömmel & Dransfeld (10) on the excitation of very high frequency sound in quartz plates and its detection by optical diffraction. The ultrasonic waves appear to be excited by the electric fields at the surfaces of the crystals, whence they propagate into the interior.

Brockhouse & Iyengar (11) showed how the frequency-wave number relation of a crystal could be measured from the energy distribution of initially monoenergetic neutrons after scattering from the crystal. The results with Ge could not be fitted to any simple models of the Born-von Karman theory, general forces out to at least third-neighbors being required.

*Critical point in the solid state.*—A critical point in the strict sense is possible only in a one-component system, but a similar phenomenon may be found in a two-component system at constant pressure. A striking property of a system near a critical point is the scattering of light known as *critical opalescence.* Recent theories predicted a virtually horizontal section in the T-C or T-P diagram in the neighborhood of $T_c$, which was observed by Rice (12) in cyclohexane-aniline. In solid solutions, critical points are not often found, because the phase change usually occurs with a change in crystal structure. Some years ago Münster & Sagel (13) began a study of critical points in binary alloys by measurements of emf., density, and conductivity. In the system Al-Zn they found no evidence for a horizontal section in the T-C diagram. The question arose as to whether it would be possible to observe critical-opalescence scattering of x-rays in these solid solutions.

The intensity of the diffuse small-angle scattering is given by

$$I_D = N\left[x_1x_2(f_1 - f_2)^2 4\pi\rho \int_0^\infty (\bar{g}_2^{(1)} - \bar{g}_{12}^{(2)}) \frac{\sin ur}{ur} r^2 dr\right]$$

where $x_1$, $x_2$ are the atom fractions; $f_1$, $f_2$ are the Fourier transforms of the atomic electron density distributions; $u = (4\pi/\lambda) \sin \theta/2$; and $\rho = N/V$ is the total number density of atoms. The x-ray scattering thus leads to the determination of $(\bar{g}_2^{(1)} - \bar{g}_{12}^{(2)})$ which is the function describing the correlation of positions between atoms 1 and 2, insofar as this is not governed by the crystal structure itself. Münster & Sagel (14) have now measured this small angle scattering down to 20′ from Al-Zn and Au-Ni (15) alloys. A marked critical "opalescence" occurred in the scattering curves, and the correlation function showed short range ordering up to 31 A at 0.5° above $T_c$. These results demonstrate that internal equilibrium is rapidly achieved in these solid phases, so that the methods of statistical mechanics are directly applicable. There has been a considerable theoretical development in the field (16).

A closely related critical phenomenon is the local fluctuation in the magnetization of a ferromagnetic material in the neighborhood of the Curie point. This fluctuation causes a greatly enhanced scattering of slow neutrons [Squires (17)]. It was suggested by van Hove (18) that the fluctuations in magnetization M changed with time according to a diffusion equation,

$\partial M/\partial t = D\nabla^2 M$. From the energy spectrum of the scattered neutrons, it is possible to calculate $D$ [Ericson & Jacrot (19)], and interesting experiments of this kind have been reported (20).

## DEFECTS

Defects in a perfect crystal structure can be classified as point defects (vacancies, interstitials), line defects (dislocations), and plane defects (grain and subgrain boundaries, stacking faults). To understand the properties of crystals it is necessary to investigate the behavior of isolated defects and then the ways in which defects interact with one another. In the case of point defects, great simplifications are possible because they can be treated statistically as analogous to solutes in a dilute solution [Kroger & Vink (21), Brebrick (22)]; such simplification is not possible for line or plane defects. Furthermore, ordinary reversible thermodynamics is often of little use in these classes, since the defect concentrations are not equilibrium properties but depend on the history of the systems.

### Point Defects

The difficult problem in the calculation of the energies of point defects has been the treatment of the relaxation energy of the crystal structure around a vacancy or interstitial, which may amount to more than half the energy needed to create the defect in an unrelaxed structure. The method originally developed by Mott & Littleton (23) has been refined by Kurosawa (24) and applied to Schottky defects in alkali halides and Frenkel defects in AgCl. Fumi & Tosi (25) have similarly calculated energies for defect formation and interaction; the energy of combination of a cation and anion vacancy was 14 kcal. in NaCl and 17 in KCl, re-emphasizing the probable importance of vacancy pairs at moderate temperatures. In a related research interactions between vacancies and impurity ions were calculated, and the experimental testing of the models by paramagnetic resonance was reviewed (26).

New calculations for defects in copper by Terwordt (27) indicated a considerably lower distortion than earlier estimates. Girifalco & Streetman (28) calculated that the relaxation around a vacancy in a b.c.c. crystal would be only about five per cent for an inverse power pairwise potential, so that the model of the relaxion, a highly relaxed disordered structure around a vacancy, was rejected for such a crystal, although it cannot yet be excluded for the alkali metals since these have a different repulsion energy. Fisher (29) computed the elastic distortions near interstitials in a b.c.c. structure and concluded that the influence of dissolved carbon in increasing the free energy of $\alpha$-iron relative to $\gamma$-iron is largely due to the elastic strain energy.

The series of papers by Seeger & his co-workers on defects and transport properties continued (30) with a general treatment of the scattering of conduction electrons.

Dryden & Meakins (31) obtained some nice measurements of dielectric losses in alkali halides due to divalent impurities and the cation vacancies they cause. Two distinct peaks in dielectric absorption were observed, the one at higher frequency $\omega$ only at high impurity levels. The absorption at lower $\omega$ could always be described by a Debye curve with a single relaxation time $\tau$, the loss factor being

$$e'' = 2\pi B\omega\tau/[1 + (2\pi\omega\tau)^2]$$

The frequency of maximum absorption $\omega_{max} = A \exp(-E/RT)$. The absorption is ascribed to the orientation of the dipole, formed by the positive impurity ion and the effectively negative associated vacancy. Two mechanisms are possible: an alkali ion can move into the vacancy or the impurity ion can do so. Both the $E$ and $A$ values agree well with those from conductivity or from diffusion of radioactive tracers, and the dielectric method appears to have good capabilities for future work.

*Thermoelectric power.*—Howard & Lidiard (32) devised a new theory for the thermoelectric power of ionic crystals, and some experimental confirmatime was subsequently obtained [Christy & co-authors (33)]. If a temperature gradient is impressed across an ionic conductor fitted with metal electrodes, the thermoelectric potential, with neglect of small terms, is $V_B - V_A = (V_R - V_Q) + \Delta\Phi$ (the first term is the homogeneous part and $\Delta\Phi$ is due to differences in contact potential). The thermoelectric power $\theta$ is $(V_B - V_A)/\Delta T$. The cases were considered of pure AgBr and AgCl, with Frenkel disorder, and the same crystals doped with $Cd^{+2}$ to introduce cation vacancies. The usual statistics were applied to the defects and the concentration expressions put into the equations for the current densities. The predicted $\Delta\theta$ for a doped as compared to a pure crystal rose sharply to about 1 $mV$/°C. for a small concentration of Cd. The equation obtained was

$$\Delta\theta = \left(\frac{\xi^2 - 1}{\xi^2 + \phi}\right) \frac{\phi(q_i^* + q_v^* + h)}{(\phi + 1)eT} - \frac{k}{e} \log \xi$$

in which $h$ is the heat of formation of a Frenkel pair, $\xi$ is the relative vacancy concentration, and $\varphi$ is the ratio of the interstitial mobility to vacancy mobility. The $q_i$ and $q_v$ are the heats of transport of interstitials and vacancies; the movement of a defect is a thermally activated process and the energy given to the defect to move it from its initial position must be returned by the defect as it reaches its final position. Thermoelectric measurements may thus give an unusually detailed insight into transport processes for defects in the solid state.

*Color centers in alkali halides.*—Many experimental studies, especially by resonance methods, have appeared since the last summarizing review of this field by Seitz (34). So many different centers have been reported that it is difficult for the outsider to follow the work without a lexicon. It may be recalled that the simplest color center, the F-center of Pohl, is almost certainly an electron bound to an anion vacancy. Electron spin resonance

showed that the trapped electron is shared between the six alkali ions surrounding the vacancy. Blumberg & Das (35) calculated the magnetic interactions of an electron at an F-center in KCl and found good agreement with the resonance data. The F′-center evidently consists of two electrons bound to an anion vacancy. The V-centers, which are often antimorphs of the F-centers, consist of positive holes in otherwise filled halide shells bound to cation vacancies and other negative traps.

Paramagnetic resonance methods are better suited to V- than to F-centers since there is a larger hyperfine interaction on the halide ion, and also the hole is more localized than the F-center electron. Känzig & his coworkers (36, 37, 38) have made detailed studies by electron spin resonance of V-centers in alkali halides irradiated at low temperatures (~20°K.) with x-rays and then slowly warmed. Most of the work was done on LiF because of the monoisotopy of F. The V-center was shown to be a $Hal_2^-$ molecular ion oriented along a [110] axis of the crystal. Thus, this center is not associated with vacancies but may be regarded as a sort of self-trapped hole, the trapping arising from the formation of a molecular bond. This center is evidently not the same as that giving the optical V band, but the optical absorption of $Cl_2^-$ in irradiated KCl has also been directly observed [Delbecq, Smaller & Yuster (39)].

Hayes & Jones (40) studied spin resonances for $Mn^{+2}$, $Co^{+2}$, and $Cr^{+3}$ dissolved in alkali halides. After irradiation with $\gamma$-rays, resonances were found for $Mn^+$, $Co^+$, and $Cr^+$, which were destroyed by annealing. This work shows that di- and tri-valent ions are effective electron traps at room temperatures, and supports the suspicion that some of the color centers that have been described in crystals from commercial sources may actually be reduced impurity ions. Rolfe (41) found hydroxide bands as a constant impurity in all synthetic crystals unless exceptional precautions were taken to dry the halides before melting.

The theoretical calculation of energies, oscillator strengths, and charge distributions for various exciton models in the alkali halides was critically considered by Dexter (42). An experimental determination of the oscillator strength $f$ for F-centers in KCl was made by Scott & Hills (43), who compared the optical absorption with the amount of hydrogen evolved on solution of additively colored crystals containing excess K. They obtained $f = 1.17 \pm 0.15$, based on the Smakula equation,

$$Nf = 0.821 \times 10^{17}[n/(n^2 + 2)^2]A \text{ cm.}^{-3}$$

where $N$ is the number of F-centers per cc., n is the refractive index at the frequency of the absorption band, and $A$ is the area under the absorption curve in ev/cm. Doyle (44) found a somewhat lower $f$ from the change in color of methyl red on solution of KCl with excess K, $0.91 \pm 0.11$, but both these new figures are higher than previous values. Bate & Heer (45) calculated the concentration of F-centers in irradiated LiF from the paramagnetic susceptibility measured with a torsion balance, and obtained $f = 0.82$.

If crystals containing F-centers are irradiated with light in the F band, coagulation of the excess metal into colloidal particles occurs in certain temperature ranges (around room T for NaCl and KCl). Doyle (46) has improved the Mie theory for the scattering of light by metal particles, and estimated the size of the Na particles in NaCl to be from 200 to 4800 atoms.

If the arrangement of defects composing a center has a lower symmetry than that of the lattice, the dipole moment associated with an optical transition of a trapped electron or hole will have a preferred orientation relative to the lattice. Such a center will absorb light most strongly if the electric vector of the light is parallel to the dipole of the center [Ueta (47)]. The dichroism produced in the absorption band of H-centers in KCl and KBr after bleaching with polarized H-band light showed that the center has a symmetry axis $\parallel$ [110], and thus eliminated previously suggested models for this center [Compton & Klick (48)]. Kanzaki (49) studied similarly the dichroism of the F and M bands. Seitz had suggested that the M-center was an electron, trapped at an aggregate of two anion vacancies and one cation vacancy. This is clearly anisotropic, but the F-center itself almost certainly has cubic symmetry. Kanzaki found that the F-band dichroism depended on the concentration of F- and M-centers in a way that indicated it was due to a spatial association between them.

*High pressure effects.*—The effects of high pressure on the optical absorption of impurities in alkali halides have been investigated by Drickamer & co-workers. In KCl doped with KCN, there are two $CN^-$ bands; the one ascribed to $CN^-$ at lattice imperfections is observed only on compression, the other is ascribed to $CN^-$ replacing $Cl^-$ at normal sites (50). The effect of pressure on the F-band is a shift toward higher energies (51). Effects on the $Tl^+$ spectrum in alkali halides were followed up to 130,000 atm. (52). High-pressure studies have also been made on Si-Ge semiconductors [Paul & Warschauer (53)].

*Faraday effect.*—Dexter (54) considered the effects of impurities and F-centers on the refractive index and the Faraday effect in ionic crystals. Although the predicted effects are very small, the extreme sensitivity of the available experimental methods suggests that valuable experiments will be possible. In semiconductors, on the other hand, the Faraday effect may be very large; it varies inversely as the square of the effective mass of the current carriers. Thus large effects should occur in a semiconductor such as InSb, in which the effective mass is only one or two per cent of that of free electrons. Moss & Smith (55) have measured the rotation of the plane of polarization of a beam of infrared radiation passing through thin plates of InSb in a magnetic field. Measurements were made over wavelengths 16 to 22 $\mu$ by means of novel polarizers made of piles of polyethylene films set at the Brewster angle. In impure n-type InSb very large effects were observed, with rotations up to 1° per $\mu$ thickness of semiconductor (about $10^4$ times a usual Verdet constant). The effect is linear with the magnetic field and occurs with negligible time delay.

## Dislocations

The theoretical properties of dislocations, their interactions with point defects and with one another, and their influence on the mechanical, optical, and chemical properties of crystals have been intensively investigated. Menter (56) has reviewed the electron microscopy of crystal lattices in an article illustrated with many beautiful photographs; the observation of dislocations by direct transmission and by the technique of moiré patterns is discussed.

The walls of edge dislocations in Ge crystals were shown to be regions of high electrical conductivity and thus their positions could be detected by potential measurements [Hogarth & Baynham (57)]. If the energies required to form positive and negative ion vacancies in an ionic crystal are unequal, the dislocations in a crystal in thermal equilibrium will be electrically charged and surrounded by a diffuse cloud of oppositely charged vacancies. Eshelby *et al.* (58) related this property to the yield stress of ionic crystals, but such models may not be adequate to the complexity of the experimental phenomena, e.g., the observations of Gorum *et al.* (59) that the ductility of ionic crystals depends on the ambient gas.

The effect of dislocations on the electric breakdown in silicon p-n junctions was studied by Chynoweth & Pearson (60). Avalanche breakdown microplasmas occurred preferentially where dislocations passed through the junctions, and there was also an enhanced internal field emission. The trend of many of these recent studies has thus been to emphasize the correlation between the mechanical and electrical strengths of solids [Vorobev (61)], and explicit evidence that dislocations are concerned in both processes was found in some striking observations by Gilman & Stauff (62) on the nucleation of dislocations by strong inhomogeneous electric fields applied to LiF, which was immediately followed by a catastrophic electric breakdown over the surface of the crystal.

The small angle scattering of x-rays or neutrons due to dislocations has been calculated by Atkinson & Hirsch (63).

The decoration of dislocations has yielded much new detailed information on dislocation patterns and networks. Amelinckx (64) described in great detail the dislocation systems in KCl decorated with silver precipitated by diffusion of AgCl followed by annealing in hydrogen. Dislocations that moved during the anneal often left traces of particles behind them, suggesting that certain parts of the dislocation lines provide more stable precipitation sites. In CsBr, decoration with colloidal gold was obtained by heat treatment with $HAuBr_4$, quenching and annealing; emergence points of individual dislocations could be observed. Castle (65) used an ingenious photolytic method to decorate single dislocations in AgCl, illumination in microsecond pulses with simultaneous application of voltage pulses to draw the photoelectrons into the crystal. A sensitive new method for revealing dislocation patterns in AgCl was described by Bartlett & Mitchell (66); the system of prismatic dislocations occurring around the precipitates suggested

an analogy with the mechanism of precipitation hardening in metals. A "decoration method" that might eventually be applicable to metals was devised by Cottrell & co-workers (67). Helium atoms were injected into copper by cyclotron $\alpha$-particle bombardment; on subsequent heating, the helium separated as small gas bubbles in those parts of the metal where the helium atoms receive vacancies from nearby sources. In this instance, these sources were grain boundaries but not twin boundaries or dislocations.

The delineation of dislocations by etch-pit patterns led to many new variations on the basic theme, e.g., selective etching of Li precipitates in Ge (68), correlation of pits and copper decoration in Si (69), and the study of pits in photographic grains (70). The mechanism of etch-pit formation by $FeF_3$ on LiF was elucidated by Gilman, Johnston & Sears (71). The $Fe^{+3}$ ions slow the motion of steps across the surface of the crystal from a nucleated pit, by forming a complex with the $F^-$ ions. Such a chemical mechanism may suggest suitable etchants for other crystals.

Both chemical and thermal etching were used by Gibbs (72) in a detailed study of three distinct dislocation systems in corundum. Deforming corundum at increasing temperatures led to a nearly random dislocation array; this was ascribed to the widespread condensation of lattice vacancies into platelets at random places: these produce dislocations under stress. The Cambridge electron-microscope group have observed such effects directly in aluminum quenched from 600° to −45°C. [Hirsch *et al.* (73)], but in gold trigonal voids are formed.

When corundum crystals were boiled in a salt solution and then heated in a device for measuring their conductance, pulses of current of about $10^9$ electrons each were detected, believed to be due to electrons left behind when positive ions were driven from the dislocations by heating [Tucker & Gibbs (74)]. Bent corundum crystals boiled in $Mg(NO_3)_2$ solution became catalysts for the decomposition of $H_2O_2$, and this catalytic activity was destroyed by heating above the range of the current pulses. These experiments suggest that the activation energy for adsorption on a surface near the end of a dislocation can be altered by the introduction of charge along the dislocation line, an interesting model for an "active center."

Gibbs & co-workers (75) discovered a remarkable electrical microstructure in corundum by coating the under sides of crystals with a metallic film and exploring the upper sides of the heated crystals with a 1 $\mu$-diameter potential probe. With probes about 10 v. negative across a 40 $\mu$ crystal, the backing metal could be pulled through the corundum, presumably along dislocation lines. The current flow was strongly temperature dependent.

## DIFFUSION

Diffusion plays a fundamental role in most rate processes in the solid state. The goal of theory is the calculation of diffusion coefficients D from structural data, but in many cases even the atomic mechanism of the elementary diffusion step is not yet clearly established. When diffusion is

known to occur through a simple point defect, as in the alkali halides, fairly good calculations of both the energy of formation of the defect and the activation energy for its mobility can be made [Fumi & Tosi (76)].

In the simplest atomic theories of diffusion, each jump of a diffusing atom is supposed to be completely independent of the preceding jumps. A more detailed examination of certain atomic mechanisms revealed, however, that this assumption was not always true, and that the direction of an elementary jump might be correlated with that of previous jumps. An instance readily visualized is in the vacancy mechanism: when an atom jumps into a vacancy, it leaves a vacancy at its former site, and its most likely next jump will be right back into the vacancy left behind. Thus a correlation factor $g$ is introduced into the kinetic theory expression for $D$, which becomes $D = gd^2\nu \exp(-E/RT)$, where $d$ is the jump distance and $\nu$ the vibration frequency. Compaan & Haven (77) have calculated the correlation factors in various crystal structures for the interstitialcy mechanism (displacement of lattice atom by interstitial according to $X_i + X_{i'} \rightarrow X_i + X_{i'}$) in a paper that also gives references to the earlier work on $g$; they provide an ingenious electrical analog network for computation of the $g$ factors. LeClaire (78) discussed chemical diffusion as a random-walk problem, and among other interesting results, showed that Onsager "cross-terms" were not primarily determined by correlation effects.

A very useful advance in the atomic theory has been made by Schoen (79) in his succinct analysis of the relation between correlation factors and isotope effects on $D$. If we compare the $D$ for two isotopes of masses $m_1$ and $m_2$, the atomic jump frequencies are nearly in the ratio $(m_1/m_2)^{1/2}$. Hence Schoen defines the strength of the isotope effect by

$$S = \frac{[D(m_1)/D(m_2)] - 1}{(m_1/m_2)^{1/2} - 1}, \quad (m_1 > m_2).$$

He distinguishes the cases of "slow" solute atom diffusion with successive jumps of solute atoms weakly correlated, and "fast" diffusion with strong correlation. For interstitial diffusion, ring mechanisms, and vacancy or interstialcy mechanisms with weak correlation, $S \cong 1$. Such cases include H in Pd and steel, Ni in Cu, and Na in NaCl and KCl. In contrast, a case with strong correlation was found in diffusion of Cd in Ag and Cu, and the isotope effect was measured with $Cd^{109}$ and $Cd^{115m}$. In both cases the $S \cong 0$, and hence $D$ depended not on the mass of the tracer but on the mass of the solvent atoms. The interstitial mechanism is definitely excluded, and the mechanism is vacancy (most likely) or interstitialcy. This new analysis of the isotope effect should make it a more useful technique for determination of mechanisms.

Several new experimental methods have been developed, based on ion emission from solids [Cornides (80)], ultrasonic relaxation times [Hikata & Lücke (81)], and the use of very low energy tracers [Mackliet (82)]. McAfee (83) obtained the $D$ for He and other gases in glass from precise measure-

ments of transient flows; he found a large reversible increase in D when the tensile stress exceeded half the breaking stress, an effect ascribed to the opening and closing of submicroscopic fissures. It would be interesting to know whether this strange phenomenon is peculiar to the glassy state. LeClaire & Rowe (84) measured the diffusion of gases not ordinarily soluble in metals by introducing the gas by an ionic bombardment; in the case of Ar in Ag the $D$, followed by irradiation analysis, had a perfectly normal value of 0.16 exp $(-33$ kcal./$RT)$ cm.$^2$sec.$^{-1}$.

Especially in the study of sparingly soluble solutes in crystals such as Ge and Si, the diffusion has been frequently measured from the rate of precipitation of solute on quenching a supersaturated solution. Ham (85) has recalculated the time dependence of such diffusion-limited precipitation for small spherical, spheroidal, and cylindrical particles of precipitate. The fraction of solute unprecipitated has the form exp $(-bt^n)$ for small time $t$. If the particles grow initially from negligible dimensions with constant eccentricity, $n=3/2$ for all spheroids, including rods and disks. Earlier formulations of this problem were hence incorrect.

*Experimental results.*—Self-diffusion in crystalline and amorphous Se was measured at low temperatures and the curious result $D=6\times10^{25}$ exp $(-53$ kcal./$RT)$ reported for the latter [Boltaks & Plachenov (86)]. Diffusion in pure single crystals was investigated by Hoffman (87) in the Ag-Ge and Ag-Tl systems. Kanter (88) found that the $D$ for $C^{14}$ in natural graphite above 2150°C. proceed with a normal frequency factor and E = 163 kcal. From irradiation experiments it appears that interstitial C is mobile in graphite even at 200°C. and thus its mobility cannot control the uptake of $C^{14}$ which was slow even at 2000°C.; a vacancy or direct interchange mechanism is indicated.

Diffusion of chloride in NaCl was measured by the rate of exchange between $Cl_2$ and NaCl crystals [Harrison, Morrison & Rudham (89)]. There were two linear portions in the Arrhenius plot; the high temperature slope of 53 kcal. was assigned to migration of anion vacancies, and Lidiard (90) suggested that the low temperature slope of 37 kcal. was due to migration of mobile pairs of + and − vacancies, an interpretation supported by further experiments (91). Tannhauser (92) reported a variable E for the diffusion of Br in AgBr over the narrow range 332–415°C.; the activation volume of 44 cc./mole from the pressure dependence of $D$ supported a vacancy mechanism.

About as nice an experimental confirmation as we should like of the theory of correlation effects in diffusion was found by Miller & Maurer (93) in the electrical conductivity $\sigma$ and the diffusion of Ag in AgBr and AgBr doped with $CdBr_2$. In the doped crystal the $Cd^{+2}$ replaces $Ag^+$, forming an equivalent number of vacancies; the ratio of the mobilities of Ag from $D$ and from $\sigma$ then had the value 1.25 predicted for the correlation factor $g$ for a vacancy mechanism in this structure. The data for pure AgBr, on the other

hand, agreed with those of Friauf (94) in giving $g = 1.8$ to 2.1, as predicted for the interstitialcy mechanism.

A conference at M.I.T. in June brought chemists, physicists, metallurgists, and ceramicists together to discuss rates and mechanisms of phase transitions, diffusion, and sintering, particularly in oxides (95). All these processes are related to the problem of diffusion of oxygen in oxides. Kingery *et al.* (96) measured $D$ for $O^{18}$ in $Zr_{0.85}Ca_{0.15}O_{1.85}$ for which there is x-ray evidence of oxygen vacancies; the activation energy of 30 kcal. agreed with that for the ionic conductivity, which seemed therefore to be due to oxide ions. Belle & Auskern (97) reported the $D$ for $O^{18}$ in stoichiometric $UO_2$ as $2.6 \times 10^{-5}$ exp $(-30$ kcal./$RT)$, but in this case there is magnetic evidence for interstitial oxygen. Both Cu and O [Moore, Ebisuzaki & Sluss (98)] diffusion have now been measured in $Cu_2O$; at 1000°C. the $D_O$ is about 1/50 $D_{Cu}$, but the activation energies are about the same, 39 kcal., which is also the $E$ for oxidation of copper; the $D_O$ increases with oxygen pressure, evidently excluding a mechanism via oxygen vacancies in this crystal. Haul & Just (99) have begun their studies of diffusion of O in oxides with CdO, and reported $E = 106$ kcal.

The mechanisms of diffusion of metal in oxides with excess metal, such as ZnO, appear to be complex. Thomas (100) found an extremely rapid diffusion of zinc into ZnO, presumably as interstitial Zn, with $D_i = 2.7 \times 10^{-4}$ exp $(-13$ kcal./$RT)$, whereas the substitutional diffusion of radioactive Zn into ZnO at higher temperatures had $D = 4.8$ exp $(-73/RT)$ [Secco & Moore (101)]. It is possible that the situation in ZnO is like that suggested by Frank & Turnbull (102) for diffusion of Cu into Ge, so that interstitial Zn can exchange with lattice Zn only in the vicinity of a zinc vacancy. Thomas (103) also determined the $D$ for In in ZnO, from the decline in the conductivity of a crystal previously saturated with In as the In diffuses to and precipitates along internal dislocation lines: $D = 2.5 \times 10^2$ exp $(-73$ kcal./$RT)$ and increases as $P_{O_2}^{1/4}$, which indicates that cation vacancies control the diffusion.

*Dislocations and grain boundaries.*—In 1957, Hart (104) suggested that dislocations in single crystals could enhance the apparent volume diffusion without sensibly altering the form of the diffusion profile, e.g., the Gaussian curve for linear diffusion from a thin source. For the measured diffusion coefficient, he derived

$$D = (s^2/2\tau)r + D_v(1 - r)$$

where $r$ is the fraction of atoms in dislocations, $s^2$ is the mean square migration in the diffusion direction of the atoms in the dislocation in a time of stay $\tau$, and $D_v$ is the volume diffusion coefficient for a perfect crystal. Tomizuka (105) obtained experimental evidence for such an effect in self-diffusion in Ag at 600°C., the first term amounting to about five per cent of $D$. Williams & Slifkin (106) found a long irregular tail on the diffusion profile in

experiments with radioactive Au of high specific activity diffusing into single crystals of Ag, which they ascribed to penetration along dislocations.

Grain boundaries, often considered as dislocation arrays, should provide another means of studying diffusion in imperfect regions of a solid, but the phenomenological theory of grain-boundary diffusion is discouragingly complex, and simplified versions contain parameters such as "grain-boundary width" that lack precise definition. Therefore one of the best procedures has been to follow the diffusion along grain boundaries visually by autoradiography. Lacombe *et al.* (107) have measured $D_v$ in monocrystals of $\alpha$-Fe and a $D_b$ for grain-boundary diffusion in polycrystals, finding $E=64$ and 45 kcal., respectively. Some of the autoradiographs are striking (108) and show clearly that diffusion along grains is a sensitive function of the grain geometry, and also that there is a slower but definite preferential diffusion along subgrain boundaries.

*Sintering.*—There seems to be little doubt that the predominant process in the sintering of powder-metal compacts, after the initial welding, is the diffusion of vacancies from voids to grain boundaries [Pranatis (109); Balluffi & Seigle (110)]. Sintering is thus closely related to the deformation of crystalline bodies under the influence of surface tensions or small external stresses. Therefore the observations of Harper (111) that single crystals of Al near the melting point deformed under small loads as rapidly as polycrystals indicated that mechanisms not involving grain boundaries must sometimes be operative. This conclusion was further supported by the observation that a void in a single crystal of Cu does shrink in annealing [Zaplatynskyj (112)].

In the sintering of oxides and ceramics, both cations and anions must diffuse. The work of Burke on alumina (113) gave a nice visual demonstration that grain boundaries were important for the elimination of voids in these systems also. Kuczynski *et al.* (114) applied his useful technique of measuring the kinetics of growth of necks between spheres and plates to the $Al_2O_3$ system. The analysis had shown that $x^n/a^m=A(T)t$, where $a$ is the radius of the sphere and $x$ that of the neck. This relation provides a test of the phenomenological mechanism: for viscous or plastic flow, $n=2$, $m=1$; for evaporation and condensation, $n=3$, $m=1$; for volume diffusion, $n=5$, $m=2$; and for surface diffusion, $n=7$, $m=3$. For the metals Cu, Al and Th, these criteria indicated volume diffusion; for glass, viscous flow; for NaCl and KCl, evaporation. For $Al_2O_3$, Coble (115) has found volume diffusion with $D=10^7 \exp(-165 \text{ kcal.}/RT)$. Kuczynski found $x^5/a^2 \sim (\gamma V/RT)Dt$, where $\gamma$ is the surface tension, $V$ the molar volume, and $D=2.5\times10^4 \exp(-131 \text{ kcal.}/RT)$.

## GROWTH OF CRYSTALS

*Nucleation.*—Some years ago, Bardolle & Bénard (116) first demonstrated how oxide crystals germinate and grow on the surface of iron. This

nucleation phenomenon has since been studied in copper, nickel, and several alloys, and it appears to be a general step in the oxidation of metals at elevated temperatures, especially at reduced pressures. More detailed results for Cu have now been obtained by Bénard & Grønlund (117); the germination appears to be an intermediate stage between the formation of a chemisorbed or very thin oxide layer and the diffusion-controlled growth of thicker layers. From the pressure dependence of the lateral growth of the germs, it appeared that the mechanism might be a chemisorption of oxygen on a $Cu_2O$ surface followed by a surface diffusion of the adsorbed oxygen to the interface of the germ.

A nucleation process with a similar mechanism was observed by Bassett (118) when small amounts of gold were evaporated onto the cleavage faces of alkali halide crystals. The nuclei of gold were taken up on evaporated carbon films and examined by electron microscopy, so that germs containing as few as 1000 atoms could be detected. Evidently gold atoms on an alkali halide are weakly adsorbed and very mobile, migrating rapidly over the surface until they attach themselves to a gold nucleus. These nuclei form along dislocations but also at other points randomly distributed over the surface.

The precipitation of Al from supersaturated solution in Si has been investigated by Rosenbaum & Turnbull (119). The number of Al particles nucleated depended strongly on the thermal history of the specimens. In specimens quenched slowly from a $T$ of homogeneity to the precipitation $T$, less than $10^6$ particles/cc. were nucleated, but in specimens rapidly quenched and preaged at a low $T$, more than $10^{14}$/cc. occurred. In this case, inoculation was believed to be due to point defects, clusters of point defects, or even homogeneous nucleation. Tweet (120) studied precipitation of Cu in Ge; at low supersaturation ratio, nucleation occurred at dislocations, but at high ratio, he also found other precipitation sites and admitted the possibility of spontaneous nucleation.

*Whiskers.*—Because of their unusual mechanical properties much attention has been devoted to monocrystalline whiskers, but the earlier view that their high strength is always due to a relative absence of edge dislocations now appears unlikely. A conference at Cambridge in March discussed the state of the field (121). The principal methods of preparation are (*a*) extrusion [Franks (122)]; and (*b*) crystal growth from supersaturated media or by chemical reactions: Ag [Courtney (123)], inorganic salts [Charsley & Rush (124)], Zn and Cd [Coleman & Cabrera (125)], graphite [Meyer (126)]. Extruded whiskers may have a high bend strength but may be weak in tension. Extremely high growth rates have been observed in extrusion, up to $10^4$ A/sec., with Sn at 7000 psi at room temperature; growth appeared to occur from the roots. Whiskers obtained by crystal growth also usually grow from the roots (but sometimes from the tips) and when small may display high strengths in both bend and tension. For example, the critical shear stress in 1 $\mu$ Zn whiskers was 100 times that of a large crystal (125). The yield curves

of whiskers are often abnormal; tiny iron whiskers sustained an elastic strain of five per cent and then suddenly broke. Even tiny crystals extracted from an alloy matrix can be very strong; Webb & Forgeng (127) obtained crystallites of $Fe_3C$, $Cr_2N$, Cr, and $Cr_3O_4$ in this way.

Screw dislocations in $Al_2O_3$ whiskers were detected by x-rays [Dragsdorf & Webb (128)]. Smith & Rundle (129) examined with x-rays the perfection of tin whiskers; these evidently contained a normal quota of dislocations, but there was no evidence that they had grown predominantly along close-packed directions around screw dislocations. Amelinckx (130), however, grew alkali halide whiskers that were very plastic and sometimes contained a hollow axial channel.

Gomer (131) developed a method for growing mercury whiskers in a modified field-emission tube. They were very strong single crystals, generally of [110] orientation, adhering strongly to a tungsten substrate. The stress along the whisker axis was obtained from $\sigma = (E/300)^2$ dyne cm.$^{-2}$ where $E$ is the electric field in volts per centimeter at the end of the whisker. Strengths up to $10^{10}$ dyne cm.$^{-2}$ were calculated, close to the value expected for a perfect crystal. The strength of adherence to the substrate must be even higher, and this is not easy to understand. The kinetics of growth of the whiskers could be followed by field measurements; the growth appeared to occur from the tips by a surface diffusion of mercury atoms impinging over the surface.

Vermilyea (132) found that electrode position on Cu whiskers occurred only at isolated sites and required the rather high overvoltage of 100 Mv. When the diameter exceeded 10 $\mu$, however, the electrolytic behavior became that of ordinary Cu. Price *et al.* (133) devised a new theory of crystal growth based on the electrolytic growth of whiskers.

Although the usual whisker may have a quota of dislocations, crystals can be grown by special methods which are virtually free of dislocations, as shown by Dash (134) for Si.

Iron whiskers are ideally suited for studies of magnetic domains and important developments have been made in this field by DeBlois & Graham (135) and by Coleman & Scott (136).

## CHEMICAL REACTIONS

The general theory of rate processes for solid-state reactions is still mostly an unknown territory, but a few interesting explorations have been made. Waite (137) has treated the problem of a reaction of the type $A+B \rightarrow AB$, occurring in a solid and controlled by the diffusion together of the reacting species. The rate of reaction is the probability rate at which a single A and B diffuse together, multiplied by the product of the numbers of A and B present at any time. Thus $A+B \rightarrow AB$ will be second order, and $A+B \rightarrow B$ will be first order, after elapsed times which are long compared to a transient explicitly expressed. The treatment of irrregular initial distributions, as

occur in the kinetics of annealing of radiation damage, was also considered. For a more general case, in which diffusion is no longer rate controlling, the reaction A+B→AB was found still to be second order, but with a time-dependent rate constant. The equations were first applied to the annealing of radiation damage in Ge, assumed to consist mainly of vacancy-interstitial pairs which diffuse together and recombine. Considering a quite different type of solid-state reaction, the oxidation of solid metals by permanganate, Hill (138) suggested that sometimes a few atoms of product can diffuse ahead through the dislocation network of the reactant and cause nucleation at new sites. Such a mechanism was called a "diffusion chain" and could provide an explicit model for certain exponential or autocatalytic reaction-time curves.

Among newer experimental methods is "matrix isolation" used by Pimentel (139) to follow reactions with an $E$ as low as 1 or 2 kcal. in a frozen solid matrix. Examples were the diffusion of $NH_3$ in solid argon and the *cis-trans* isomerization of $HNO_2$ at 20°K. Klein & Scheer (140) allowed H atoms from a hot filament to impinge on condensed films of olefines at 78°K.; the atoms diffused rapidly through the solid hydrocarbons and appeared to react in two steps: addition of H to olefine to form an alkyl radical, followed by addition of a second H to saturate the radical. Willard & coworkers (141) summarized the effects of phase on some reactions caused by radiation in organic compounds. In the radiolysis of isopropyl iodide and photolysis of ethyl iodide, the rates are about tenfold higher in the solids at 78°K. than in the liquids at room temperature.

*Tarnishing and gaseous corrosion.*—The oxidation of Ta from 50–300°C. was followed by a new capacitance technique [Vermilyea (142)], and was found to be adequately represented by the rate law $dn/dt = a \exp(b/n)$, where $n$ is the number of oxygen atoms reacted. This is the equation derived by Cabrera & Mott (143) from the assumption that the removal of an ion from the metal is rate determining. On the other hand, Law (144) found that the uptake of oxygen by evaporated silicon surfaces, after the rapid formation of a monolayer, followed $dn/dt = AP^{1/2} \exp(-Bn)$ from 0 to 50°C. The activation energy $E$ depended on the extent of uptake, and was 5.8 kcal. at the monolayer point. The same rate law, sometimes called the Elovich equation, has turned up quite frequently in both chemisorption and oxidation [cf., the review by Landsberg (145)]. In the present system, its simplest basis would be an activation energy increasing linearly with the uptake, $E = E_1 + nE_2$. Only for very small $n$ would the Cabrera-Mott equation agree formally with the Elovich equation.

When the product layer on a metal has become markedly thicker than about 1000 A, as in oxidations at high temperatures, the rate of growth is usually controlled by diffusion of reactants, and $dn/dt = K/n$, the parabolic rate law. Wagner (146) devised a successful theory for the rate constant, $K$, which is based on the assumption that during the course of reaction an

equilibrium is maintained at the metal-oxide and oxide-oxygen interfaces. Although parabolic oxidations are not usually proceeding close to equilibrium, the equilibrium theory may still be valid since the affinity falls gradually across the product layer, and for each elementary diffusion step $\delta A \ll kT$. In the cases of oxygen-excess oxides such as $Cu_2O$, NiO, CoO, and FeO diffusion occurs predominantly via cation vacancies, but only indirect evidence was available regarding the vacancy gradient in the oxide layer. Engell (147) has now devised a sensitive electrometric method for determining the excess oxygen in FeO and applied it to sections from the FeO layer on Fe, quenched rapidly from the oxidation reaction. He found that as long as the oxide layer was firmly adherent, there was a linear gradient of cation vacancies and the vacancy concentrations at the phase boundaries were close to their equilibrium values. Thus this system appeared to agree in detail with the theoretical model of Wagner.

The oxidation of titanium was measured from 300–1000°C. and the results were complex indeed, four different rate laws occurring as the temperature was raised [Kofstad, Hauffe & Kjöllesdal (148)]; the parabolic law between 600–850° was ascribed to diffusion of O through $TiO_2$. Kofstad (149) devised a convenient method for determining the activation energies of oxidation reactions, based on a single run at a linearly increasing temperature. The oxidation of niobium was also complex [Gulbransen & Andrew (150)].

Wagner (151) gave a valuable comprehensive analysis of the factors governing the oxidation of alloy systems, which will serve as a guide for much future work in this field.

The plasticity of a hot oxide layer is an important factor determining its adherence to a metal, and catastrophic or "breakaway" oxidation is beginning to be considered in a more fundamental way. Gulbransen & Andrew (152) studied the phenomenon with Zr-Sn alloys, and Jaenicke & Leistikow (153) measured directly the mechanical stresses in oxide layers on copper during oxidation and reduction.

The oxidation of Cu, Al, Fe, Zn, and Mn in a glow discharge was measured volumetrically and with a quartz beam microbalance [Nazarova (154)]. With current densities of 0.06 to 0.6 m.amp./cm.$^2$, the Cu anode oxidized according to a cubic law, $dn/dt = K/y^2$, and the other metals, a logarithmic law $dn/dt = K/t$; with Cu, $Cu_2O$ formed at the anode and CuO at the cathode. Trillat & co-workers (155) observed a rapid oxidation of metals bombarded with energetic ions from air, and the nitridation of nickel in a beam of ions from a nitrogen discharge.

## RADIATION EFFECTS IN SOLIDS

The effects of high energy radiation on solids have been comprised under the term "radiation damage" because they almost always add to the difficulties of operating nuclear reactors, causing expansion of fuel elements, em-

brittlement and enhanced corrosion of cans, and a decrease in the strength of structural materials. These effects are due to the displacements of atoms from normal lattice sites, with subsequent formation of various kinds of defects, so that the phenomena after the primary irradiation stage are closely related to the statics and dynamics of defects that have already been considered.

The theory of radiation damage and hardening in metals has been discussed by Seeger (156) in a comprehensive paper that reviews and correlates much of the work on this subject, particularly for the metal copper, which has been studied in most detail. The "first stage" in any complete theory would be the calculation of the numbers of defects of various kinds generated under different irradiation conditions from a detailed knowledge of the interaction potentials between the different particles involved. Such a theory is only in its infancy, so that a "second stage" of theory must intervene, the calculation of how the various defects influence measurable properties of the solid materials. The property most frequently used to study radiation damage has been *electrical resistivity*, which is easy to measure even during an irradiation, but is unfortunately difficult to calculate and does not distinguish in a sensitive way between various kinds of defects. Measurements of stored energy, volume expansion, and changes in lattice parameters can be calculated readily but are also insensitive. Seeger believes one of the most useful properties will be the critical shear stress of metals, as used in the work of Blewitt & his co-workers (157). The "third stage" in the development of the theory, however, has been so far the most actively pursued; this is the study of how the physical effects produced during irradiation anneal out upon subsequent thermal treatment. The anneal at lowest temperatures has been the most difficult to interpret. Seeger believes that from about 25°–50°K., the rapid anneal is due to recombination of close pairs of interstitials and vacancies and atomic rearrangements in the zones at the ends of the paths of fast displaced atoms (thermal spikes).

In the paper *On the Interpretation of Radiation Effects in Noble Metals* by Holmes & co-authors (158) the analysis differed in important details from that of Seeger. No definite evidence was found for effects due to thermal spikes, and the annealing at the lowest temperatures was ascribed to interstitial migration over appreciable distances. The experiments on electron bombardment of copper at 12°K. by Corbett & Walker (159) were cited. Electron bombardment is a mild procedure compared to irradiation with heavy particles, and no thermal spikes would be expected. The recovery curve showed four distinct regions between 20° and 65°K., and there is little doubt that the annealing processes are very similar to those after heavy-particle irradiation, e.g., by deuterons [Magnuson *et al.* (160)]. Simmons & Balluffi made an x-ray study of the lattice expansion of Cu (161).

*Nonmetals and compounds.*—An excellent review of radiation effects in nonmetallic solids was given by Crawford & Wittels (162). Among the most

remarkable effects are the radiation induced transformations of $ZrO_2$ and $BaTiO_3$ from stable to metastable structures. The effects of irradiation on $\alpha$-quartz attracted special interest because of the extraordinary decrease in density at saturation, 14.7 per cent. Wittels examined the details of the lattice expansion caused by neutron irradiation. For exposures less than $3\times10^{19}$ fast neutrons per cm.$^2$, the expansion resembles the ordinary thermal expansion; above this level, distortion commences and amorphous regions make their appearance, as severe anisotropic shear strains are caused by crowding of oxygen interstitials into the open *c*-axis channels of the structure; for doses in excess of $1.2\times10^{20}$, only the glassy structure remains. Stevens *et al.* (163) measured the magnetic susceptibility of irradiated quartz, finding a maximum concentration of magnetic defects at an exposure of $4\times10^{19}$n/cm.$^2$, which may correspond to the maximum number of broken bonds.

Lithium fluoride has been a favorite subject for neutron irradiation since $Li^6$ has the enormous capture cross section of 950 fermi: $Li^6+n^1\rightarrow H^3$ (2.7 Mev)$+He^4$ (2.1 Mev). Three kinds of defects are produced at each capture, $H^3$, He, and $Li^+$ vacancies, in addition to the effects due to the 4.8 Mev energy, enough to produce about 1500 defect pairs per fission. Thus about one per cent of all the atoms in LiF can be displaced by an integrated flux of only $10^{18}$ cm.$^{-2}$. (Lithium might be used as a sort of irradiation catalyst.) Smallman & Willis (164) allowed irradiations to continue until a majority of the ions had been displaced. Most of the defects in LiF anneal out from 300–500°C., but dislocations, clusters of point defects, and cavities were formed at various stages of the anneal [Gilman & Johnston (165)]. Lambert & Guinier (166) concluded from the x-ray scattering of irradiated LiF that interstitial Li coagulated into definite layers parallel to [100] planes. Irradiation of LiF with electrons hindered the glide of dislocations, an observation consistent with the hardening previously noted [Whapham (167)].

The decomposition of solid nitrates by x-rays was investigated by Cunningham & Heal (168). Most of the $NO_3$ dissociated to $NO_2$ and O at normal lattice sites, and the rate of decomposition depended on the ability of the O to move away through the cage of ions. For $KNO_3$ below 50°C. the *G* (number of molecules decomposed per 100 ev energy) was about two, but *G* rose with temperature, as was consistent with the need for some thermal activation energy to separate the primary products. The *G* for $KNO_3$ was about 100 times *G* for $LiNO_3$, with the other alkali nitrates in between; this effect was correlated with the "free space" in the structures.

An interesting interplay of adsorption and radiolysis was observed when *n*-pentane was adsorbed on silica gel and then irradiated with x-rays [Caffrey & Allen (169)]. The extent of decomposition was greatly increased compared to that in the pure liquid, and a specific transfer of energy from the silica to the adsorbate was suggested. Different adsorbents gave different products, all differing from those from the liquid alone. Maurin, Ballantine & Sucher (170) found that irradiation of oxide catalysts with $\gamma$-rays could markedly

increase their activities for the *ortho-para* hydrogen conversion, by factors approaching one hundredfold.

Because of the extensive use of graphite in reactors, its responses to irradiation have been studied in some detail. Exposure of natural graphite crystals to $5\times10^{20}$ nvt thermal neutrons increases their burning rate about threefold. The oxidation causes pit formation on the cleavage faces of irradiated crystals, and the increased burning rate is caused by these pits [Hennig, Dienes & Kosiba (171)]. The pits are believed to start at vacancies created by the irradiation.

Because of continuous generation of defects, diffusion rates in a solid undergoing irradiation may be greatly enhanced. The theory for diffusion in a medium with a constant rate of generation of defects has been worked out by Dienes & Damask (172) for three different annealing mechanisms, bimolecular recombination of vacancies and interstitials, linear flow of defects to surfaces and dislocations, and both these mechanisms combined. Measurements on $\alpha$-brass agreed well with the linear annealing mechanism.

### Sputtering

Any energy less than 50 kev might be called "low" in the jargon of radiation effects, but it is in this range that many of the most interesting chemical processes are to be found, after the first wild rush of the incident particle has slowed to a pace at which it begins to nod to its neighbors. One can also utilize directly slower particles, from ion sources or discharge plasmas, which in this case do not penetrate below the superficial layers of the solid. Here they cause the phenomenon called "sputtering"; miscalled perhaps, since the word connotes a mass transfer like fat from a frying pan, whereas all the evidence indicates that the particles driven off have the dimensions of atoms or at most small molecules. This erosion of solid surfaces by ionic or molecular bombardment has recently attracted more intense interest, since it appears that the materials research for nuclear fusion and jet propulsion will require a detailed knowledge of the resistance of solids to very hot gas streams and discharge plasmas. A comprehensive review of the subject up to 1955 was given by Wehner (173).

Historically, there have been two basic theoretical models for the sputtering process: (*a*) In the vaporization theory, the incident ion causes a local hot spot in the solid from which vaporization occurs; the sputtering rate therefore should depend only on the energy of the incident particles, and not on the ratio of their mass to that of the target atoms. (*b*) The momentum theory envisages elastic impacts between incident ions and atoms in the solid, which transfer momentum to the latter. The target atoms may be driven forth by the initial impact or by subsequent collisions between displaced atoms. In this model, the sputtering rate depends on the mass ratio of ion and target atoms. Most recent analyses have been based on the momentum theory. Keywell (174) obtained equations for the sputtering

coefficient $\theta$ (atoms sputtered per incident ion) by analogy with neutron diffusion in a moderator. Thommen (175) refined the method of Keywell to obtain

$$\theta = (E_o/E_d)\Phi(M_1/M_2)$$

where $E_o$ is the energy of the incident ion, $E_d$ is the energy of sublimation of the solid, and $M_1$, $M_2$ are the respective masses of ion and target atom. The function $\Phi$ is defined by a rapidly converging series with one term for each collision of the decelerating ion. The resulting function represented quite well the form of the experimental curves of $\theta$ vs. $M_1$, $M_2$ for rare gas ions with $E_o \ll 8$ kev incident on PbS, Ge, and $FeS_2$, if it was assumed that only the first collision was effective, i.e., that sputtering was a true surface phenomenon.

The models of Keywell and Thommen assumed hard sphere collisions and no energy transfer to the electrons in the solid. Except for hydrogen ions the latter condition is probably valid below 10 kev. Langberg (176) treated the collisions as Morse curve interactions, and obtained results that were in good agreement with data on the energy threshold for sputtering found by Wehner (177) for $Hg^+$ ions on metals. Whereas Langberg assumed that the ejecting collision was always between two target atoms, Henschke (178) assumed it was always between a deflected ion and a target atom. It is hard to say which theory is more suitable without further experimental data. Silsbee (179) considered the collision problem in more detail and concluded that energy pulses would be preferentially propagated along close packed lines of atoms in the solid. The many difficulties of the surface processes were avoided by Goldman & Simon (180) who worked out a theory applicable above 50 kev, where the incident ions penetrate so deeply that most sputtered atoms come from a narrow region below the surface. They found $\theta \sim M_1 \log E_o/M_2\, E_o \cos \psi$, where $\psi$ is the angle between the incident beam and the normal to the target surface. Data are nonexistent so far in the range of $E_o$ covered by this theory.

The earlier sputtering data were usually obtained by immersing the target directly in the plasma, or using the unanalyzed output from ion sources; but recently measurements have been made with analyzed ion beams. Rol, Fluit & Kistemaker (181) have used the Amsterdam isotope separator to study the sputtering of copper by $Ar^+$, $Si^+$, $N^+$, and $N_2^+$. In the case of $Ar^+$ normally incident on Cu, the $\theta$ rises to 6.0 at 10 kev and then remains practically constant to 25 kev; at 40° incidence, $\theta$ is 10.5 at 10 kev. Radioactive targets were used to allow the detection of amounts of silver as small as $10^{-8}$ gm. sputtered by beams of $H^+$, $H_2^+$, and $D^+$ [O'Briain, Lindner & Moore (182)]. At 10 kev, the values of $\theta$ were about an order of magnitude lower than those previously cited for hydrogen ions, and the difference was ascribed to the absence of atoms from the analyzed beam.

Most of the particles driven off on sputtering are neutral atoms of the

target material, but a mass spectrometric study by Honig (183) showed that some positive and negative ions of the target were sputtered when Ag, Ge, and Ge-Si were bombarded with rare gas ions between 30 and 400 ev. Species such as $Ag_2^+$, $Ag_3^+$, $Ge_2$, $Ge_2^+$ could also be detected in lesser concentrations. Wolsky (184) made a microbalance study of the ionic bombardment of Ge by $Ar^+$.

When clean Ni was bombarded with H ions, no excess H was introduced; but, if the Ni was coated with NiO or BaO, an increase of several orders of magnitude in the concentration of dissolved H was obtained [Morrison & Lander (185)]. The H ions appear to penetrate the oxide layer and become trapped beneath it. In the case of ZnO, excess H concentrations were produced $10^5$ times higher than normal, which indicated a surface barrier of about 15 kcal. to the escape of H from the crystals [Lander (186)].

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# NUCLEAR AND PARAMAGNETIC RESONANCE[1,2]

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## INTRODUCTION

This review is almost exclusively restricted to a discussion of electron spin resonance, and is concerned primarily with the ESR of free radicals. The cursory treatment given nuclear resonance results from the nature of the authors' interest and competence, but it is hoped that this brevity will be at least partially mitigated by the forthcoming appearance of two books on the subject that are scheduled for publication before the present review. These texts are: J. D. Roberts, *Nuclear Magnetic Resonance*, and Pople, Schneider & Bernstein, *High-Resolution Nuclear Magnetic Resonance*. Ingram has written a book on the ESR of free radicals which, although received too late for review, appears to be a comprehensive treatment of the subject (1).

Two reviews on electron resonance have appeared: one, by Honerjäger (2), is an elementary and superficial account, and a second, by Whiffen (3), deals briefly with the ESR of free radicals. A review entitled *Nuclear Magnetic Resonance in Chemistry* has been presented by Labhart (4), and collections of symposium papers include a special Chemical Society publication (5) and a New York Academy of Sciences monograph (6).

## ELECTRON SPIN RESONANCE

### Free Radicals

*Aromatic radicals in solution.*—A number of interesting theoretical and experimental studies of free radicals have been reported. The spectra of aromatic radicals in liquid solution exhibit an isotropic proton hyperfine splitting that is a direct measure of the unpaired electron-spin density at the site of the particular proton giving rise to the splitting. As a first approximation, the odd-electron in these radicals may be considered to be in a $\pi$-type molecular orbital and, therefore, no direct hyperfine structure arising from protons lying in the plane of the aromatic ring is expected. Although it is now well known that a $\pi$-$\sigma$ interaction accounts semiquantitatively for the experimental results, there has been considerable interest in the detailed relation of the odd-electron density measured at the proton to the unpaired-electron density distribution throughout the rest of the molecule. In 1956, McConnell had suggested (7) that there was a direct proportionality between the proton splitting and the density of the unpaired electron on the adjacent carbon in the aromatic ring but, at that time, there was little experimental or theoretical justification for this proposal. McConnell & co-workers (8 to

[1] The survey of the literature was completed January, 1959.

[2] The following abbreviations will be used: ESR (electron spin resonance); NMR (nuclear magnetic resonance).

11) have since made a thorough and elegant theoretical investigation of this relationship that shows it may indeed have considerable validity in a modified form, and significant experimental data pertaining to the question has been obtained by Weissman *et al.* (12, 13, 14). Incidentally, McConnell (8) also concludes that isotropic spin-orbit coupling contributes a negligible amount to proton hyperfine interactions in typical aromatic radicals.

De Boer & Weissman (13) have shown that McConnell's original, unmodified proposal may be valid in certain molecules. They have studied a large number of mono-negative and mono-positive ions of aromatic radicals including condensed-ring systems (naphthalene, anthracene, perylene, pyrene, etc.); biphenyl and terphenyl; and a few multi-ring compounds containing methylene bridges. One of the most significant results of their work is the beautiful proportionality, within a single even-alternate hydrocarbon, between the proton hyperfine splittings and the total density of the unpaired electron on the adjacent carbon atom as calculated by the Hückel molecular-orbital theory. In a number of molecules, well-resolved spectra were obtained which allowed a fine-grained intercomparison between calculated and experimental splittings, and in other compounds, although the resolution was insufficient for detailed verification of this proportionality, the results were consistent with a proportionality. However, in one even-alternate hydrocarbon studied, the pyrene negative ion, the hyperfine pattern could not be explained on the basis of the calculated electron-density distribution. Odd-alternate hydrocarbons were not studied by these authors, but a few nonalternate molecules were investigated. The odd-electron density calculated for the nonalternate hydrocarbons from the Hückel theory is not expected to be as reliable as that for alternate hydrocarbons but, nevertheless, reasonable agreement with experiment is obtained for the negative ions of fluoranthene and acenapthylene. The negative and positive ions of acepleiadylene, however, yield results which are not in agreement with the splittings predicted from the Hückel-type calculations. Theoretical studies of electron-spin densities in alternate hydrocarbon ions have been made by Hoijtink (15).

Tuttle & Weissman (14) have obtained the spectrum of the benzene negative ion. It shows that the six protons are coupled equally with the odd electron and therefore they conclude that the expected Jahn-Teller distortion must be a more rapidly changing phenomenon than the characteristic time (of the order of $10^{-7}$ sec.) of the hyperfine interactions. A recent study of the Jahn-Teller theorem has been made by Longuet-Higgins *et al.* (16).

De Boer & Weissman (13) point out that if there were a single constant of proportionality for all C—H bonds in aromatic molecules relating the odd-electron density in the ring to the proton splittings, the total extension in magnetic field of the spectrum for one ion could be calculated from the total extension of the spectrum of any particular ion such as, for example, the benzene negative ion. Their data show, however, that the proportionality varies from one compound to another by as much as 50 per cent even though

there is, in most cases, a proportional relation for the protons within a given even-alternate hydrocarbon.

Another very interesting observation results from the work of de Boer & Weissman: in sulfuric acid solutions of the aromatic molecules, free radicals are produced which exhibit essentially the same ESR spectra as the corresponding negative ions. The molecular-orbital theory of alternate hydrocarbons predicts that the density of unpaired $\pi$-electrons should have the same distribution in the positive and negative ions, and the authors therefore concluded that sulfuric acid must oxidize the hydrocarbon to the monopositive ion. The positive-ion spectra in sulfuric acid exhibited greater splittings and narrower line widths than observed in the spectra of the negative ions in tetrahydrofuran.

Tuttle & Weissman (14) have found that the ESR spectra of the anions of toluene and the xylenes, unlike the ions of the unsubstituted even-alternate hydrocarbons, do not conform to a simple theoretical picture of proportionality between odd-electron density and proton splitting. Methyl-substituted compounds, such as the methyl-substituted semiquinones (17, 18), usually show a splitting attributable to the methyl groups of the same order of magnitude as the ring splittings, but in the methyl-substituted anions studied, only the *m*-xylene shows any indication of methyl-group-proton hyperfine structure. The variation of methyl-proton splitting within this series of compounds is not the only surprising result: the ring-proton splittings in the toluene anion must be interpreted as arising from equivalent protons in the ortho and meta positions, and the spectra of the *o*- and *p*-xylene anions are very similar to the spectrum of the toluene anion. Although Tuttle & Weissman conclude it is possible to construct one-electron Hückel-type molecular orbitals of the proper symmetry to describe an odd-electron density consistent with the ring splitting in the toluene and *p*-xylene ions, no such orbital could be constructed to account for the splittings in the *o*-xylene.

The preceding discussion indicates that although there are compounds for which McConnell's original proposal of proportionality between odd-electron density and indirect proton hyperfine interaction appears to hold, there are several examples in which it is inadequate. Other evidence which shows the partial inadequacy of the original proposal arises from studies of substituted semiquinones (17), in which the variation of splitting was found to be much too large to be accounted for in terms of a variation of odd-electron density, but the most obvious difficulty is found in the spectrum of compounds like triphenylmethyl. Brovetto & Ferroni (19) were the first to suggest that the indirect proton hyperfine interactions could be both positive and negative, and were able to interpret the triphenylmethyl spectrum using this idea and a valence-bond theory of odd-electron density distribution. Brovetto & Ferroni's work has thus indicated the necessity of calculating "spin density" rather than odd-electron density. The former can be either positive or negative with respect to the polarization of the total

$z$-component of spin, and McConnell & co-workers (8, 9), in their highly significant extension of Brovetto & Ferroni's work, have suggested a modified proportionality relation of the form $a_N = Q\rho_N$. Here, $a_N$ is the hyperfine splitting arising from proton $N$, $Q$ is a semiempirical constant, and $\rho_N$ is the unpaired *spin* density (rather than odd-electron density) at carbon atom $N$ bonded to proton $N$. The authors (8) state, with reference to the approximations needed to obtain this relationship, that "we suspect (it) is a good approximation in general, but . . . (it) really needs detailed quantitative calculations for verification."

The negative spin densities needed to explain the ESR spectra of odd-alternate radicals result from a standard valence-bond treatment, but a simple one-electron molecular orbital theory always predicts a nonnegative spin density (10). If the $(2n+1)$ carbon atoms in an odd-alternate hydrocarbon are numbered from 1 to $2n+1$, valence bond theory predicts negative spin densities at the positions of the even-numbered atoms (8, 10). Molecular-orbital theory with $\pi$-$\pi$ configuration interaction can also lead to negative spin densities, but obviously the valence-bond theory is simpler; and the rather good agreement between Hückel-type molecular-orbital calculations and experimental splittings found by Weissman *et al.* in many even-alternate radicals, implies that negative spin densities are relatively unimportant in these compounds. Negative spin densities might, however, account for the differences in the total extension in field observed among these various radical ions (10, 13). Of course, deviations from proportionality between splittings and spin density may arise from approximations implicit in the calculation of the spin densities as well as from a possible inexactness in the fundamental proportionality relation (10).

McConnell & Chesnut (8) conclude that the sign of the indirect hyperfine interaction ($Q$ in the above relation) is negative, so that the spin polarization at the proton is opposite in sign to the net spin polarization of the radical. Adam & Weissman (12) have, in fact, concluded from experimental studies that a negative sign is most likely. Their study was on the anisotropic splitting due to $C^{13}$ in the methyl position of triphenylmethyl present in dilute solid solutions of triphenylmethyl in triphenylamine. These authors include in their calculations a twisting of the phenyl groups out of the plane by a rotation of 30 degrees.

McConnell *et al.* have given detailed calculations of spin densities in the allyl radical (8, 11, 20) and in the perinaphthenyl radical (10). Inclusion of $\pi$-$\pi$ overlap in the theory has been made possible by introducing the concept of "spin density matrices" (20), and McConnell concludes that an empirical value of $Q$ in the above relation, good to about 10 per cent, is $Q = -23$ gauss or $-63$ Mc./sec.

McLachlan (21) has made a valence-bond study of the splitting arising from the protons in a methyl group bonded to an $sp^2$-hybridized atom containing an unpaired $p$ electron. Methyl splitting has been previously studied by Bersohn (18), who used a molecular-orbital theory. McLachlan proposes a relationship of the form $a = Q\rho$ where $a$ is the splitting constant arising

from the methyl proton, $\rho$ is the spin density on the radical-containing atom to which the methyl group is attached, and the parameter $Q$ is 28 gauss. He concludes this splitting is positive whereas the indirect splitting on ring protons is negative. A somewhat similar calculation of methyl-group splitting by Chesnut (22) is discussed below.

Adam & Weissman (23) have reported the observation of the spectrum of the sodium ketyl of benzophenone in dimethoxyethane. They find a complex pattern which includes a splitting from the $Na^{23}$ nucleus, and conclude from studies of the variation of the spectrum with benozphenone concentration that, in the exchange reaction between the ketyl and benozphenone, the electron is transferred as a sodium atom, i.e., both the electron and sodium nucleus go together.

Other studies of free radicals in solution include those of Ward & Klein on the nitrobenzene negative ion (24), and of a large variety of semiquinone radicals by Adams, Blois & Sands (25). The splitting patterns obtained by the latter authors are not fully interpreted in many cases and, for certain of the spectra presented, the nature of the radical species is highly uncertain and cannot be the obvious semiquinone intermediate. Hervé (26) has studied the dependence of the line width of benzene solutions of diphenylpicrylhydrazyl on concentration. Other work on the quenching of hyperfine structure was performed by Hausser (27) on N-ethyl phenazyl and 1:3 bisdiphylene-2-phenyl allyl. Bersohn has calculated the spin densities in hydrazyl and picryl-N-amino carbazyl (28). Studies of $R_2NO$ radicals indicate an intermolecular interaction in solution and a solvent effect on the g-value (29, 30). Effects of oxygen on the spectra of diphenylpicrylhydrazyl have been examined (31, 32).

Blume has performed ESR spin-echo experiments (33) on sodium-liquid ammonia solutions at low fields, finding that $T_1$ and $T_2$ are equal to within about 10 per cent. This result amplifies earlier work of Hutchison *et al.*

Bird, Baird & Williams (34) have studied the spectra of $NO_2$ (in equilibrium with $N_2O_4$) in $CCl_4$ and $CS_2$ solutions. They resolve a hitherto undetected hyperfine splitting, and conclude that the splitting corresponds to a surprisingly large amount of nitrogen-2s character, namely 18 per cent of that for a pure nitrogen-atom 2s electron.

*Triplet states.*—Numerous investigators have tried to confirm, by ESR, the detection of triplet states in condensed phases, particularly the triplet states of phosphorescent organic molecules in rigid glasses at low temperature (1). Although susceptibility measurements of fluorescein in boric acid glass have shown paramagnetism on ultraviolet irradiation, ESR measurements have been negative. Hutchison & Mangum, however, (35) have recently found an ESR spectrum from naphthalene when single crystals of the solid solution in durene are irradiated with ultraviolet light at liquid-nitrogen temperature. They observe an orientation-dependent spectrum arising from a zero-field crystalline anisotropy occurring at fields extending over a range of 2100 gauss and are able to evaluate the parameters in the spin Hamiltonian. (The authors have indicated that signs given in the original paper

for these parameters should be reversed.) The cause of the large anisotropic splitting, which had been predicted by Weissman to explain the previous negative results (36), is undoubtedly the spin-spin interaction between the two unpaired electrons in the triplet. Weissman (37) has made rough estimates of the dependence on tumbling frequency of the motionally-narrowed line width and spin-lattice relaxation time ($T_1$) arising from the dipolar interaction, and concludes that a narrowing of the line width from 2000 to 20 gauss would require a tumbling rate in excess of $10^{11}$ c.p.s. The relaxation times are estimated as a function of the average effective interaction-distance between the two electrons, and Weissman concludes that relaxation times comparable to those normally found in solutions of radicals at room temperature (about one microsecond) are only obtained if the electrons are fairly far apart or if their distribution about each other is highly symmetrical. An effective distance of 6 A would produce a relaxation time of from 0.1 to 0.01 $\mu$sec. These results show why experiments on randomly oriented triplet molecules in solids give no detectable ESR spectrum, but indicate why triplet molecules in solution, such as the Chichibabin hydrocarbons, in which the effective inter-electron distance may be large, can give rise to well-resolved spectra. Other explanations (1) put forward to account for the failure to detect triplet-state molecules must be considered untenable. Bersohn (38) has developed a semiempirical theory of the spin-spin splitting which predicts the variation of the parameters in the spin Hamiltonian for a series of aromatic hydrocarbons.

Gutowsky *et al.* (39) have examined a number of photochromic solids but only one exhibited an ESR spectrum. Hirshberg & Weissman (40) examined low-temperature solutions of irradiated bianthrones and spiropyrans but detected no ESR spectra. If these molecules are in triplet states, the conclusions of the previous paragraph should be applicable.

*Trapped radicals.*—A number of investigations of radicals formed and trapped in rigid matrices by a variety of means have been reported. The spectra, although found to be characteristic of the particular system and experimental conditions, are only interpretable in terms of a definite radical species in a few of the simplest cases, and considerable unverifiable speculation about them has appeared.

The work on atoms is, of course, the most readily subject to interpretation. Jen *et al.* have extended their work on hydrogen and deuterium atoms (41) and have also examined the spectra of nitrogen atoms (41, 42) at 4.2°K. The effect on the spectra of matrices of $H_2$, $CH_4$, and Ar (and for N atoms, also $N_2$) were observed and, although the variation in g-value is small, the hyperfine coupling constant does depend somewhat on the matrix, particularly for N atoms. The widths and shapes of the lines, as well as saturation and rate-of-passage phenomena, are discussed. Cole & McConnell (43) have re-examined the spectrum of nitrogen atoms in a molecular nitrogen matrix and have resolved four additional satellite lines not previously observed. These lines are interpreted as arising from a zero-field axially symmetric crystal-field splitting of the $^4S_{3/2}$ ground state of the nitrogen atom.

Jen's group (44) has also studied $NH_2$ and $ND_2$ radicals. These were produced by ultraviolet photolysis of the appropriate isotopic species of ammonia and were trapped in an argon matrix at 4.2°K. Interpretation of the spectra shows a surprising and unexplained result: the hyperfine coupling constant for the nitrogen atom is about 12 per cent larger in $ND_2$ than in $NH_2$. McConnell (45) has pointed out that the approximately equal intensity of the proton triplets (1:1:1 instead of a 1:2:1 pattern), observed in this $NH_2$ experiment, is possibly accounted for by assuming free rotation of the $NH_2$ in the matrix and a consequent symmetric proton-spin wave function with a proton-spin angular momentum of $I=1$. Other work at 4.2°K. on the radicals produced by subjecting ammonia to an electric discharge is reported by Cole & Harding (46).

Smaller & Matheson (47) have examined the radicals formed from a variety of alkanes, olefins, alcohols, and ethers on irradiation with $Co^{60}$ $\gamma$-rays at low temperatures. They have verified the four-line spectrum for methyl radical, and find a total spread of about 80 gauss for the pattern in a methane matrix. Jen *et al.* (41) have also made a careful study of the methyl radical and find a hyperfine coupling constant of about 65 Mc./sec. (the exact value depending on the matrix). This number should be compared with the value of 63 Mc./sec. deduced by McConnell in interpreting indirect proton splitting (8). McConnell's group (48) obtained the methyl radical by x-irradiation of $CH_3I$ at 77°K., and have used samples containing $C^{13}$. The hyperfine splitting constant obtained for the $C^{13}$, namely 41 gauss, as well as Jen's result for the proton splitting, is considered by the authors to be consistent with the interpretation of the methyl radical as an at least very nearly planar molecule.

Smaller & Matheson (47) have also obtained spectra for the ethyl radical in a variety of matrices and find a quartet of triplet lines. The quartet presumably arises from the methyl protons (splitting constant about 26 gauss), and the triplets presumably arise from the methylene protons (splitting constant about 20 gauss). The spectra observed seem to be more reasonable for the ethyl radical than those reported by previous investigators (49). Environmental effects may seriously alter the nature of these spectra, however, and it is not possible to conclude that Gordy's spectra (49) do not arise from the same radical. Chesnut (22) and McLachlan (21) have given theoretical treatments of the splittings involved in these aliphatic radicals. Chesnut assumes that the methylene group can be treated as a planar $\pi$-electron system (like the -CH fragment treated by McConnell in discussing aromatic molecules), and then deduces the methyl splitting by using the theory of hyperconjugation in a manner similar to that employed by Bersohn for the semiquinones (18). Chesnut's results are in order-of-magnitude agreement with the results of Smaller & Matheson, as well as the data on other aliphatics. He also concludes that the coupling is not appreciably diminished when more than one methyl group is hyperconjugated to the central carbon atom, a deduction consistent with Bersohn's calculations (18) and the experimental results on methyl-substituted aromatics (1, 17, 50). For the indirect

hyperfine interaction arising from aromatic-ring protons, however, McConnell's theory predicts, if negative spin densities are neglected, that the total extension in field of the spectra should be approximately independent of the number of protons. These two mechanisms of interaction, indirect and hyperconjugative, can thus give different results; and one would expect the extension of the spectra of aliphatic radicals to increase with the number of groups hyperconjugated to the carbon atom containing the unpaired $\pi$ electron.

Only a few other investigations have allowed unequivocal interpretation of the nature of the radical species trapped. Grant, Ward & Whiffen (51) have used selective deuteration to identify the radical produced by $\gamma$-irradiation of glycollic acid (combined with a study of the calcium salt). The authors conclude that the radical trapped is the carboxyhydroxy methyl radical, and that the odd electron interacts strongly with only a single methylene proton. Bennett *et al.* have performed isotopic substitutions on the radicals produced on irradiation with 2 Mev electrons of caproamide and caprolactam (52), and for the caproamide have made a reasonable identification of the radical present.

Jen *et al.* (41) have examined spectra obtained from the discharges from hydrogen and hydrogen-oxygen systems, and have studied trapped $NO_2$ radicals. They were unable to observe spectra from trapped $O_2$ and NO, and resonances from oxygen and chlorine atoms were sought but not found.

Fujimoto & Ingram (53, 54) have studied the resonances produced in several monohydroxy alcohols containing small amounts of hydrogen peroxide when irradiated (*in situ* in the spectrometer cavity) with ultraviolet light. The radicals are presumably produced by attack on the alcohol by hydroxyl radicals formed from photolysis of the hydrogen peroxide but, although the resonances found are characteristic of a particular system, no definite identification of the radicals could be made. The authors studied the effects, which were quite marked, of changes in duration of irradiation and temperature of the matrix, the latter presumably affecting, among other things, the extent of motional narrowing of the lines. Several workers have studied the effects of different matrices on trapped radicals (41, 42, 47).

Whiffen's (55, 56, 57) and Ingram's (58, 59) groups have studied radicals in polymerization systems using a number of different approaches. The latter group has studied the radicals retained in the solid aggregates which separate out of monomer-polymer-solvent mixtures at sufficiently high degrees of polymerization. Radicals were also produced by photolysis of emulsions of hydrogen peroxide in pure monomer frozen to a partially crystalline solid at 90°K., and the spectra are attributed to the OH-containing monomer radical. The difference between the presumed monomer and the polymer spectra are interpreted by postulating that one of the methylene hydrogens in a polymer radical of the form $RCH_2\dot{C}(X)CH_3$ ($X=CN$ or $CO_2CH_3$) is sterically hindered by the inability of the polymer chain to rotate and therefore does not interact with the unpaired electron. On the other hand, Whiffen's group (55) studied the spectra of radicals obtained by irradiation of

polymethylmethacrylate and related materials with $\gamma$-rays and 2 Mev electrons, and suggest that the spectra can be explained if, in addition, unequal coupling of the three methyl-group protons is assumed. At present it seems that the evidence is insufficient to conclude that either of these tentative suggestions is to be preferred to the other or, for that matter, that some entirely different explanation may not be necessary. These authors (55) also showed that the polymethylmethacrylate spectrum was independent of the nature of the ester group, but did depend on the substituent on the alpha-carbon atom, and the work indicates that the polymethylmethacrylate spectrum arises from a single species of radical, albeit one present, perhaps, in different conformations.

These groups have also examined the effects of oxygen (56, 58) and of temperature (58). A kinetic study has been made on the copolymerization reaction of methylmethacrylate and glycol dimethacrylate for a photochemically initiated polymerization (57).

Gordy's group has continued its examination of the difficult-to-interpret spectra of radicals produced by x-irradiation of amino acids (60) and peptides (61).

Resonances in carbonized materials, charcoals, and petroleum have been studied by a number of authors (59, 62, 63, 64).

Trammell, Zeldes & Livingston have made a theoretical study of the satellite lines observed in atomic hydrogen spectra obtained from irradiated acids (65). They conclude the satellites arise from a weak magnetic-dipole coupling between the electron spin and a neighboring nuclear spin.

### Ions of Metallic Elements

Ôno & Ohtsuka (66) have extended the work of Bagguley & Griffiths (67) on the paramagnetic resonance absorption spectra of single crystals of $CuSO_4 \cdot 5H_2O$ and $K_2CuCl_4 \cdot 2H_2O$ to millimeter wavelengths so as to obtain better resolution of the two lines arising from the two inequivalent $Cu^{++}$ ions per unit cell than is possible at centimeter wave lengths. The shape of the absorption lines was found to vary remarkably with orientation of the crystal in the magnetic field, and a particularly interesting feature was the consistently larger intensity of the high field line in comparison to that of the low field line. The observed line shapes were interpreted in terms of exchange interaction and the frequency of exchange coupling between the $Cu^{++}$ ions was calculated using the theory of Anderson.

In exact analogy to the situation with copper acetate monohydrate (68), the paramagnetic resonance absorption spectrum of copper propionate monohydrate (69) has been interpreted by means of an effective spin Hamiltonian with an equivalent spin $S = 1$. It is assumed that each of the magnetic complexes in this crystal consists of a pair of strongly interacting $Cu^{++}$ ions.

Vacancies associated with a divalent cation which has replaced a univalent cation in a crystal lattice have been studied in $Cu^{++}$-doped AgCl (70) and in $Mn^{++}$-doped NaCl (71). The existence of bound vacancies has been verified for both of these cases at low temperatures, but the ESR spectra are

strongly temperature dependent and indicate that the vacancy complexes are not stable at room temperature. The $Cu^{++}$-doped AgCl spectra was interpreted by assuming that there are three types of inequivalent $Cu^{++}$ centers in these crystals.

The ESR spectrum of a paramagnetic ion in a single crystal is usually interpreted in terms of a spin Hamiltonian of appropriate symmetry. This procedure has been carried out for $Mn^{++}$ in hexagonal ZnS using a crystalline field of symmetry $C_6$ (72), for $Mn^{++}$ in hexagonal ZnO and CdS using a crystalline field of symmetry $C_{6v}$ (73); for $Eu^{++}$ in $CaF_2$ using a cubic crystalline field (74, 75); for twelve rare earth ions and $Np^{+3}$ substituted for $La^{+3}$ in the anhydrous $LaCl_3$ structure using a crystalline potential of symmetry $C_{3h}$ (76); for $Gd^{+3}$ in the triclinic $LaCl_3 \cdot 7H_2O$ crystal (77), and for diluted erbium and neodymium magnesium nitrate using a crystalline electric field of predominantly icosahedral symmetry (78). Two groups have investigated $Gd^{+3}$ in $CaF_2$: Low (79) concludes from the spectra that the $Gd^{+3}$ is on a site of cubic symmetry but the Oxford group interprets the ESR spectrum as indicating a tetragonal crystal field (75). Low suggests that the discrepancy may arise from differences in sample preparation.

The signs of the cubic-field splitting constant and the hyperfine interaction constant for $Mn^{++}$ in cubic ZnS originally reported (80) have been found to be in error (81) and, with the correct sign, the data are in agreement with Watanabe's theoretical treatment (82).

The original crystal-field theory of Bethe and Van Vleck requires modification when the bonding between the central ion and the ligands is partially covalent, and appropriate theories were developed several years ago by Stevens (83) and Owen (84). These authors predict a reduction in the effective spin-orbit coupling constant (as compared to the value for the free ion) and in the nuclear hyperfine splitting constant. The extent of the partial covalent bonding has been examined in several salts: Maki & McGarvey have investigated copper (II) bis-salicylaldehyde-imine (85) and copper (II) bis-acetyl-acetonate (86), and Jarrett has studied copper dimethylglyoxime (87). A considerable amount of covalent bonding is reported for the $Cu^{++}$ in these compounds. Low has investigated both the ESR and the optical spectra of $Co^{++}$ and $Ni^{++}$ in MgO single crystals (the paramagnetic ions are in cubic crystalline fields) (88, 89), and concludes there is partial covalent bonding. The spectrum of $Mn^{++}$ in $CaF_2$ shows a very small cubic Stark splitting and a fluorine hyperfine structure which indicates some covalent bonding with the fluorine ligands (75).

The paramagnetic resonance spectra of $Fe^{+3}$ and $Cr^{+3}$ in single crystals of $SrTiO_3$ have been investigated (90, 91). Both trivalent ions occupy $Ti^{+4}$ sites. $SrTiO_3$ is cubic above 100°K. and tetragonal below this temperature. The spectra were studied in both phases, and in the cubic phase there is indication of partial covalent bonding. The electron spin resonance observed in single crystals of $BaTiO_3$ in the ferroelectric phase is interpreted as arising from an impurity of $Fe^{+3}$ ions at titanium sites (92, 93, 94).

The ESR spectra of single crystals of NaF containing, respectively $Mn^{++}$, $Cr^{+3}$, $Co^{++}$, and $Ni^{++}$ in .01 per cent molar concentration have been studied both before and after irradiation with x-rays, $\gamma$-rays, and electrons (95). The irradiation apparently causes a reduction in the oxidation state of the paramagnetic ion; lines due to $Cr^{+}$ and $Ni^{+}$ have been observed. The spectrum of $Mn^{+}$ was not found after irradiation, although the $Mn^{++}$ spectrum is reduced in intensity by about 90 per cent. The $Cr^{+}$ and $Ni^{+}$ lines showed well-resolved fluorine hyperfine structure.

O'Reilly (96) has investigated the ESR spectrum of vanadyl etioporphyrin I dissolved in benzene and in a high viscosity petroleum oil obtaining, in the two different solutions, a motional average and a static average, respectively, of the anisotropic splitting. The results are interpreted to give the coefficients in an axially-symmetric spin Hamiltonian.

Paramagnetic resonance of rare earth ions with an even number of $4f$ electrons and an integral value of angular momentum is of interest because the degeneracy may not be completely removed by the crystal field. This degeneracy is accidental and is quite different from the Kramers degeneracy. The spectra of the tri-positive ions of Pr, Pm, Tb, Ho, and Tm, in single crystals of the ethyl sulfate diluted with either La or Y have been investigated by Baker & Bleaney (97). In order to interpret the observed spectra, a crystalline electric field of $C_{3h}$ symmetry is assumed, but a term must be added to the spin Hamiltonian which represents the effect of random local departures in the crystal from the normal symmetry. The nuclear spin and magnetic moments of $Pr^{141}$, $Tb^{159}$, and $Ho^{167}$ and the electric quadrupole coupling constant of $Ho^{167}$ are reported.

A study of the magnetic resonance of $MnAu_2$ as a function of temperature and the magnitude of the constant applied field has been carried out by Asch & Meyer (98). In different regions, $MnAu_2$ is antiferromagnetic, ferromagnetic, and paramagnetic.

Schneider & Weiss (99) have studied the spectrum of $[Co(NH_3)_5O]_2HSO_4 \cdot 2SO_4 \cdot H_2O$ and, although full interpretation was not possible, believe the evidence indicates that the electron is on the Co and not on the O.

Park (100) has measured the magnetic dipole and electric quadrupole moments of $Dy^{161}$ and $Dy^{163}$ by examining the ESR spectrum of $Dy^{+3}$ in crystals of yttrium acetate and lanthanum magnesium nitrate.

Abraham *et al.* (101) have shown that the spin of $Np^{239}$ is not 1/2, as first reported, but instead must be greater than 1/2. The hyperfine structure of tetravalent $Tc^{99}$ in single crystals of $K_2PtCl_6$ was resolved at liquid helium temperature. Ten strong lines are observed and the nuclear spin of 9/2 for $Tc^{99}$ is confirmed (102). The g-value and hyperfine splitting constant are reported.

The fine structure observed superimposed on the $Mn^{++}$ hyperfine lines in the spectrum of $Mn^{++}$ in $ZnF_2$, interpreted as an isotropic fluorine hyperfine interaction, has been investigated by Mukherji & Das (103). These authors calculate the isotropic splitting, and obtain fair agreement with experiment.

Calculations of the cubic crystal field splitting for $Gd^{+3}$ by Lacroix (104) indicate that the ground state may not be $4f^7(5s^25p^6)$ but perhaps $4f^6(5s^25p^66p)$.

An extensive review of crystalline field theory, with the emphasis on modern developments, and in particular on the effects of partial covalent bonding of the paramagnetic ion, has been given by Ballhausen & Liehr (105). The nature of the electron orbits in tetrahedral inorganic complexes of the first transition series is described. Estimates of the covalent character of the tetrahedral $CuCl_4^{=}$, $CoCl_4^{=}$, $MnO_4^{-}$, and $CrO_4^{=}$ ions are given and compared with data from paramagnetic resonance experiments.

A review of the effect of cubic crystalline fields on the ions of the iron group and $S$-state ions of the rare earth group has been given by Low (106). Studies of both the ESR and optical spectra, principally in the cubic crystal MgO show that nearly all the ions investigated have considerable covalent bonding.

*Instrumental developments.*—Abraham, Ovenall & Whiffen (107) have described a magic-tee crystal spectrometer similar in many respects to the commercially available Varian Model V-4500 instrument. The latter instrument has been modified for the inclusion of high-frequency field modulation by Bennett, Hoell & Schwenker (108). Misra (109) has described a heterodyne spectrometer using a matching cavity in the bridge circuit, and Marx & Bruma have discussed a klystron frequency-control circuit (110).

*Optical pumping.*—Optical pumping has recently been developed as a means of obtaining low-field magnetic splittings of atoms. Illumination with the appropriate resonance radiation is used to "pump" atoms out of one or more hyperfine sublevels, and the spins of the atoms become partially "aligned." Application of an *r-f* field of appropriate frequency causes depolarization of some of the atoms, thus enhancing the absorption of the resonance radiation. The decrease in transmitted radiation is used to detect the occurrence of the hyperfine transition.

Various studies have been made on the relatively field independent $\Delta F=1$, $\Delta m_F=0$ transitions for use in frequency standards. These include the work of Bell & Bloom (111) and Arditi & Carver (112) on $Na^{23}$, and Arditi & Carver (113) and Beaty & Bender (114) on $Cs^{133}$. $Cs^{133}$ was also investigated by Diamond, Legendre & Skalinski (115). Kastler *et al.* (116) have studied the effect of foreign gases on the $\Delta F=0$, $\Delta m_F=1$ transitions of $Na^{23}$ by measuring the polarization of the scattered light. This technique was employed to perform (117) the first NMR experiment of a singlet state on $Hg^{201}$, obtaining the splittings of the nuclear levels of $Hg^{201}$. Pebay (118) has studied the $6^3F_4$, $7^3P_2$, $7^1D_2$ metastable states of Hg produced by electron bombardment. Franken & Colegrove (119) have obtained the spectrum of the metastable helium $^3S$ state by alignment in a helium discharge.

Dehmelt (120) showed that the spin transitions of free electrons could be detected by monitoring the intensity of the sodium resonance radiation transmitted by the partially aligned sodium vapor. Transitions of the electrons cause transition of the sodium atoms by collision. This indirect method

was used by Novick & Peters for rubidum (121); Holloway & Novick for atomic nitrogen (122); Franken, Sands & Hobart for potassium (123); and Anderson, Pipkin & Baird for atomic hydrogen (124). The unstable species were produced by electric discharges in all cases.

## NUCLEAR MAGNETIC RESONANCE

General discussions of nuclear magnetic shieldings have been given by Stephen (125, 126), Glick & Ehrenson (127) and Ito (128). Magnetic shielding studies of specific molecules include: $H_2$ (129), the haloalkanes (130), and the H atom (131). Pople (132) and McWeeny (133) discuss theories of aromatic ring currents. Johnson & Bovey (134) have calculated NMR shielding values for aromatic hydrocarbons.

Theoretical studies of spin-spin interactions have been made by Stephen (135) and Hoffman (136). The use of $C^{13}$ to analyze spin-spin splittings between equivalent protons is described (137), and low field studies of spin-spin couplings have been made (138, 139). Spin-spin splitting in methanol has been analyzed (140). The evaluation of matrix elements for spin-spin coupling is discussed (141), and nuclear spin coupling by electron orbital polarization is considered (142). Calculations of $J_{HD}$ in the HD molecule have been made (143). In another of their series of papers on the analysis of NMR spectra, Abraham, Pople & Bernstein discuss molecules with four magnetic nuclei of the type $AB_3$ (144).

Shoolery & Rogers have catalogued many features of the spectra of 47 steroids (145). They find axial and equatorial protons are shifted apart by as much as 20 c.p.s. Lemieux & co-workers also find differences in axial and equatorial protons and are able to determine the effects of orientation on the chemical shifts of protons in several substituent groups (146). These results have been used to determine configurations (147). A number of studies of shifts arising in *cis-trans* isomerization have been made (148, 149), and steric effects of halogen atoms on ortho protons have been considered (150). Other uses of NMR in structural analysis and, conversely, the determination of effects of structure on the NMR spectra, include references (151 to 157). Work has been done on di-substituted (158) and tri-substituted (159) benzenes. The spectrum of liquid propane has been described (160, 161). Detailed studies are reported of 1:1:2-trifluoro 1-bromo 2-chloroethane (162), of azulene and acepleiadylene (163), of *p*-flouroaniline (164), and of some fluorine derivatives of toluene and benzotrifluoride (165). Other organic molecules for which NMR spectra have been investigated are sulphamic acid (166), diacetylhydrazine (167), some simple cyclic ethers and ketones (168), and some aromatic carbonium ions (169).

Rate and equilibrium studies using NMR include an investigation of proton transfers in acetylacetone, in di- and tri-ethyl amine (170), the nitrogen inversion rates of N-substituted aziridines (171), and the dissociation constant for heptafluorobutyric acid (172). Kinetic studies of the triiodide equilibrium (173) and of the exchange between hydrogen peroxide and water

(174) have been reported. Theoretical studies of the influence of reaction rates on NMR were made by Kaplan (175, 176) and McConnell (177).

NMR spectra of metal-acetylacetonates (178) and of mercury-olefin addition compounds (179) have been described. Evidence relating to the symmetry of $SF_4$ obtained from the NMR spectrum is reported (180). Decaborane (181) and halogen-substituted boranes have been studied (182). NMR has been used to investigate $BF_3$-alcohol complexes (183) and other co-ordinate complexes formed by $BF_3$ (184). Tiers has proposed the use of tetramethyl silane as an internal reference for the measurement of chemical shifts (185). Chemical shifts and line widths in aqueous iodide solutions were studied (186), and chemical shifts in $Pb^{207}$ compounds have been tabulated (187). Resonance shifts in $MnF_3$ have been found to be paramagnetic (188), while the shifts in several alloys are diamagnetic (189). Shifts arising in paramagnetic metal aromatic complexes (190) and from hyperfine interactions in paramagnetic solutions (191) are discussed. Low temperature studies of proton shifts in nickel salts (192), and anisotropy in the $C^{13}$ shift in single crystals of calcite (193) have been reported. Single-crystal NMR spectra have been obtained for trichloracetic acid (194) and $(CuSiO_3 \cdot H_2O)_6$ (195). NMR of molten thallium salts has been described (196). An extensive study of the NMR spectra of cesium halides has been reported (197). The spectra of compounds of the B-subgroup metals is discussed (198).

Studies have been made of hydrogen bonding and chemical shifts in gaseous and liquid hydrides (199), and of hydrogen bonding in ethanol (200) and acetic acid (201). Associative effects were also examined in *t*-butanol (202) and in KF solution (203). Hydrogen bonding in solutions of $H_2O$ and $CH_3OH$ in acetone and dimethyl sulfoxide was investigated both by NMR and by studying the heats of mixing of these solutions (204).

Line widths and second moment measurements have been used to study the structure and molecular motions in cobalt complexes (205) and in solid cyclopentene (206); to study the structure of nitroguanidine (207); of some peroxy salts (208); and of the hydrates of molybdenum trioxide (209). Andrew & Newing (210) have shown that molecular rotation in solids narrows the NMR spectrum but also produces weak side spectra. If these side spectra are included, the invariance of the second moment is preserved. A detailed theory of the saturation behavior of magnetic resonance lines has been given by Tomita (211) and measurements of line shapes of Li metal and $CaF_2$ crystals by Holcomb (212) are in good agreement with this theory. Das' theory of the vibratory rotatory motion of water molecules in hydrated crystals has been extended (213), and studies of the effects of zero-point vibrations and their relation to the determination of structural data from NMR spectra of ammonium halides and related compounds is discussed (214). NMR has been used to examine phase transitions in thiourea (215) and in 2,2-dinitropropane (216). Quadrupolar-broadened lines in polycrystalline solids have been examined (217). Exchange broadening in semiconductors has been observed (218), and the effect of pressure on the spectrum of solid hydrogen is reported (219).

Theoretical studies of quadrupolar relaxation (220), of NMR relaxation of three- and four-spin molecules in a liquid (221), and of the theory of viscosity and diffusion in relation of NMR (222, 223) have been made. The theory of the tunneling frequency of methyl groups and its relation to $T_1$ has been investigated (224). The theory of exchange narrowing has been studied (225).

Spin-echo measurements have indicated a spin exchange induced by mechanical rotation of a solid (226). Experiments in which the proton NMR frequency can be made to coincide with the chlorine frequency are described (227), and some novel spin-lattice relaxation mechanisms in solids are proposed (228).

Side-band techniques for measuring relaxation times are described (229). Relaxation-time studies on $I^{127}$ in KI crystals (230, 231), on aqueous manganous solutions (232), on metallic cadmium (233), and of water adsorbed on silica gel (234) have been made. The effect of particle size on relaxation time has been investigated (235).

Double nuclear-magnetic resonance has been used to narrow NMR lines by several authors. Certain general considerations are given by Bloch (236), Saito (237) and Bloembergen (238). The technique has been applied to the spectrum of formamide (239) and to the $Na^{23}$ resonance in NaF (240).

The proton gyromagnetic ratio has been determined with great precision (241), and recent work indicates that the previously reported values of the nuclear magnetic moments of $Pt^{195}$ (242) and $Pu^{239}$ (243) are in error.

A steady-state free precession technique for observing nuclear resonances has been described by Carr (244). The advantages are similar to those of the "spin-echo" method.

Primas has described a side-band modulation system useful in high-resolution NMR (245); field homogenizing has been discussed by Golay (246); sweep calibration by Collins (247); and pulse and spin-echo equipment by Buchta, Gutowsky & Woessner (248) and Meiboom & Gill (249). Improved Pound-Knight-Watkins spectrometers are described by Mays, Moore & Shulman (250) and by Blume (251). Other instrumental papers are given in references (252, 253).

## DOUBLE RESONANCE AND OVERHAUSER EFFECT

In recent years, various methods have been proposed for dynamic nuclear orientation by radio frequencies, notably by Overhauser (254), Feher (255), and Abragam (256). A general discussion of these techniques is given by Pipkin & Culvahouse (257), who used all of the different methods in an investigation of the radio frequency orientation of $As^{76}$. Feher has reviewed his method of electron nuclear double resonance and applied it to the determination of the ratio of hyperfine interaction constants for the isotopes $Sb^{121}$ and $Sb^{123}$ (258, 259). Electron nuclear double resonance techniques have also been used to study Nd (260), and F centers in LiF (261). Abragam & co-workers have reviewed the theory and have extended their investigations of the Overhauser effect to LiF (262, 263), to $Si^{29}$ (264) and to charcoals (265).

Codrington & Bloembergen have investigated the Overhauser effect in aqueous $Mn^{++}$ solutions (266). Erb, Motchane & Uebersfeld describe an apparatus for double resonance experiments and have used it to study fluids adsorbed on charcoals (267 to 270). Other work in this area includes references (271 to 276).

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# HIGH TEMPERATURE CHEMISTRY[1]

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Since the last review of high temperature chemistry (1) activity and publication in this field have increased tremendously. The upper limit of attainable temperature has been extended to several hundred millions of degrees and interest ranges from the preparation of new chemical substances to protection of a re-entering nose cone into our atmosphere to the production of power via nuclear fusion reactions.

The extremes of temperatures available are now so great that large concentrations of atoms and molecules may be obtained in electronic states other than their ground states, and reactions which are anomalous for the ground state may be quite logical for the excited states. For example, the inert gases may be excited to electronic configurations such that molecule formation is possible, contrary to their usual inert nature. In a sense, the periodic table of the elements which is generally useful for prediction of chemical properties are ordinary temperatures and pressures where only ground electronic states are stable is taking on new dimensions as extremes of temperature and pressure are becoming attainable.

Because of the basically different sorts of chemical species involved and different types of reactions observed, it is convenient to divide the temperature range into "high temperatures" (up to 10,000°K), "very high temperatures" (10,000° to 50,000°K.), and "extremely high temperatures" (above 50,000°K.). In the lowest temperature range one finds many complex molecules, diatomic molecules, atoms, and a few ions. From 10,000° to 50,000°K. there is little evidence for molecules more complex than triatomic, but diatomic species, atoms, and many ions are important. Above 50,000°K. the main species are ions and bare nuclei. Conventional studies of macroscopic systems in static equilibrium are usually not possible except below 5000°K. Complex flow systems, with nonequilibrium distributions of energy, in flames, shock tubes, and electric discharges are typically those in which temperatures greater than 5000°K. are attained. It is often hard to specify a unique temperature for such a system.

It is now apparent that besides the basic work on identification of high temperature gaseous and solid species, there has been a broad development of methods for measuring and attaining high temperatures, for studying the kinetics of high temperature reactions, for determination of structural parameters of high temperature species, and for practical high temperature syntheses. In addition, there has been assembled a large amount of useful data regarding physical and thermodynamic properties at high temperatures. These topics will be discussed here. Vapor pressures and phase equilibria in high temperature systems are discussed by Porter (2).

[1] The survey of literature was completed on December 31, 1958.

The proceedings of three recent symposia on high temperatures contain many excellent articles (3, 4, 5) and recent reviews have also appeared (6 to 9).

## New Methods for Measuring and Attaining High Temperatures

Either measuring or attaining a high temperature involves some sort of energy exchange between the system under study and its environment. From the viewpoint of classical thermodynamics, the nature of this exchange process—the kinetic and molecular effects—was not important; but the experimental techniques which have now been developed make it possible to ask—and answer—detailed questions about these processes.

*Measuring high temperatures* (10, 11, 12).—The best technique for measuring temperature depends on the nature of the system. For a macroscopic sample of solid, liquid, or gas one usually measures a physical property like volume, pressure, or electrical resistivity. An experimental temperature scale is defined by international agreement (13) but is subject to continuous reexamination (14). The standard for experimental thermometry is the gas thermometer, and special construction is necessary for systems at high temperatures (15). Fixed points on the experimental temperature scale have been checked by Moser, Otto & Thomas (16) and by Oishi, Awanto & Mochizuki (17). Appreciable deviations from the 1948 International Temperature Scale were observed, and there is a great need for reproducible temperature standards in the range 1000–5000°K. The positive crater of the carbon arc, the melting points of metal oxides, and certain stars are possible standards. A carbon black body for laboratory calibration of a grating spectroradiometer has been used up to 2700°K. (18).

A variety of new thermocouple materials, including oxides, carbides, and borides, have been suggested for high temperature measurements (11, 19 to 25). Errors in high temperature thermocouples caused by interdiffusion at the hot junction have been considered by Mortlock (26). Rabinowicz, Jessey & Bartsch (27) have constructed a Pt resistance thermometer for study of transient high temperature phenomena in shock tubes. Hot wire techniques have been discussed by Hoenig (28). Resistance characteristics of a number of refractory materials have been reported at high temperatures (29 to 35).

Temperature determinations based on radiation measurements are also very common for solids and gases, even up to extremely high temperatures, and the optical pyrometer has become a standard instrument for the high temperature laboratory. Lack of eye sensitivity and differences between observers have led to increased interest in photoelectric pyrometers (36 to 39). Two-color, three-color, and six-color pyrometers, and two-temperature pyrometers have been considered. There has also been a considerable development of infrared pyrometry (40 to 43). A basic difficulty lies in the attainment of true black body conditions and in the evaluation of emissivities for nonblack-body radiators. Special techniques are used for flames (44, 45). Emissivity data at various temperatures have been reported for Fe, Co, and

Ni (46); Re (47); $Al_2O_3$ (48); and for various refractory compounds and alloys (49 to 54). Dehn (55) has developed a radiation detector for measuring rapid fluctuations of temperature. Raizer (55a) has considered temperatures and equilibria in the fireball of an atomic fission explosion.

Benedek & Kushida (56) have developed a nuclear quadrupole resonance thermometer theoretically capable of a precision of $\pm 0.001°$ at 1000°C.

In an assembly of molecules or atoms the temperature determines the distribution over energy levels at equilibrium. Chemically reacting systems proceed from a group of equilibrium systems at one temperature to a group of equilibrium systems at some other temperature through various non-equilibrium configurations. Shuler, Montroll & co-workers (57 to 60) have treated these processes theoretically. Herzfeld (61) has considered the kinetics of the equilibration processes which are typical of those occurring in flames and discharges.

Ramsey (62) has introduced the concept of negative temperature to describe a system for which the population of high excited states exceeds that of lower or ground states (63, 64). Spectroscopic determinations of temperature based on a Boltzmann distribution over vibrational, rotational, or electronic energy levels are reported for spark and glow electric discharges (65 to 68), for iron and carbon arcs (69, 70), and for flames (71, 72). These same techniques have been used for various stellar systems (73, 74, 75). The problems associated with such measurements are reviewed by Huldt (76).

Radiation temperature measurements on shock waves have been reported by Model (77). Arc temperatures have been determined from shock velocities through the plasma (78).

At temperatures of 10,000°K. and higher, one may use the spectral line broadening as predicted by the Holtsmark theory (79, 80, 81). Drummond (82) has proposed a microwave thermometer for temperatures from tens of thousands to tens of millions of degrees Kelvin. Accardo (83) has suggested that $Be^7$ serve as a thermometer in the million degree range based on the temperature dependence of the electron capture decay process.

*Attaining high temperatures.*—The attainment of high temperatures by chemical means involves the production of a large amount of heat and formation of stable product gases. Since CO and $N_2$ are the most stable diatomic molecules known, one expects the oxidation of carbon-nitrogen compounds to produce high temperatures. $C_2N_2+O_2$ at one atm. yields a flame at about 4800°K.; $C_4N_2+O_2$ provides a chemical method for 5000–6000°K. (84). When $O_3$ is substituted for $O_2$, the flame temperature rises (85). In addition, one may operate under pressure and increase the temperature (86). Other high temperature flames include $H_2+F_2$ (87); powdered metals: (Al, Zr, etc.) $+O_2$ or $O_3$ (88 to 91); and $HCN+F_2+O_2$ (92).

Solar mirrors (93 to 96) and arc-image apparatus (97, 98) have been used for temperatures up to 3500°K. Small regions of solids and liquids may be heated to high local temperatures by ultrasonics (99).

A limiting factor in attaining temperatures much above 3000°K. by

resistance heating has always been that most materials melt or lose their strength at ordinary pressures. Hall (100, 101, 102) has described apparatus for attaining apparent temperatures of 10,000°K. by resistance heating in systems at very high pressures. Under such conditions, the graphite-diamond, hexagonal-BN to cubic-BN (103), and quartz-coesite (104, 105) transitions will occur. Other workers have described apparatus for production and measurements on high temperature—high pressure systems (106, 107, 108)—and a bibliography of high pressure work is available (109).

Temperatures from a few hundred °K. to over 30,000°K. have been attained by means of shock waves (110). The region heated is small and is cooled rapidly after the wave passes (111), but spectroscopic observations indicate the temperatures reached. In addition, one can frequently obtain spectra of gaseous molecules created at the high temperature (112); in one case, vaporization of powders lying on the bottom of the shock tube was reported (113). Sage & Longwell (114) have used a "ballistic piston" to attain temperatures over 5000°K.

Conn (115) and others (116) have made extensive studies of exploding wires as a means of getting high temperatures. Fischer (117) has produced temperatures of 250,000°K. in high pressure, short pulse length capacitor discharges. Finkelnberg (118) has discussed the characteristics of constricted arc systems and plasma jets at temperatures up to 50,000°K. Giannini (119) has described a commercially available plasma jet.

Temperatures considerably above 100,000°K. begin to be of interest in connection with the initiation of nuclear fusion. In terms of energy units, 1 electron volt of energy corresponds to 11,600°K., and thus "high temperature" particles are easily created by high voltage accelerators.

For the reaction ${}_1D^2+{}_1T^3\rightarrow{}_2He^4+{}_0n^1+17.6$ Mev, the "ignition" temperature above which more energy is liberated than is lost by radiation is 45,000,000°K. The reactions ${}_1D^2+{}_1D^2\rightarrow{}_2He^3+{}_0n^1+3.2$ Mev (or to yield ${}_1T^3+{}_1H^1+4.0$ Mev) require an ignition temperature of 400,000,000°K. None of the methods cited so far is sufficient. Some consideration has been given to the use of explosives to produce for at least a short time temperatures high enough to start a fusion reaction (120). An electrical discharge or a magnetic compression or a combination will definitely produce thermonuclear neutrons, evidence of some fusion; but continuous operation for power production has not been accomplished.

Chief among the techniques for attaining plasma temperatures of millions of degrees are (*a*) the pinch effect [Colgate & Furth (121)], in which the magnetic field created by a flow of current constricts the conducting plasma and raises its temperature; (*b*) the "stellerator" device of Spitzer (122), for confining and constricting a plasma with an externally imposed magnetic field; (*c*) the magnetic mirror and adiabatic compression technique (123); (*d*) the molecular ion ignition scheme with magnetic mirror confinement (124); (*e*) the shock wave plus magnetic mirror confinement (125); and (*f*) the "Astron" device for confinement and heating with a sheath of high energy

electrons (126). The details regarding the attainment of high temperatures in electrical discharges with fusion as an objective have been reported at the 1958 Geneva Conference and are discussed generally by Teller (127) and by Bishop (128), and in greater detail by various authors (129 to 135). Scott (136) has prepared a bibliography on controlled thermonuclear processes.

## Kinetics of High Temperature Reactions

*Gas-gas reactions.*—Flames are typical systems for high temperature kinetics studies, but they are hard to understand. Their complexity is now being thoroughly explored with the aid of mass spectroscopy (137 to 140) and optical spectroscopy (141 to 145), which show up appreciable concentrations of gaseous hydroxides and ions (146). Temperature distributions may be obtained and experimental and theoretical flame velocities correlated (147, 148, 149). The effect of irradiation on flames has also been studied (150).

For simpler systems, one can excite mixtures of gases or dissociate pure gases in a shock tube and determine the dissociation energy and the rate of reaction (151, 152, 153). For example, $Br_2$ dissociation and recombination have been observed by Palmer & Hornig (154, 155); $I_2$ dissociation and the decomposition of $N_2O_5$ have been studied by Davidson & co-workers (156, 157, 158); and $O_2$ dissociation has been studied by Glick & Wurster (159). Bauer & associates have studied the kinetics of formation of OH radicals in water at 2400–3200°K. (160).

The kinetics of the important reaction $N_2+O_2=2$ NO has been investigated between 2000 and 3000°K (161, 162). The kinetics of air dissociation at high temperatures has been considered by Feldman (163). A static system was used by Rosser & Wise (164) to study the gas phase oxidation of $NH_3$ by $NO_2$ over the range 600–800°K.

A flow system has been utilized by Graven (165) to study the kinetics of the $H_2$-$I_2$-HI system over the range 600–775°C. Levy (166) has used a flow system to examine the high temperature kinetics of the $H_2+Br_2$ reaction between 600 and 1470°K. Plooster & Garvin (167) have studied explosions in $H_2$-$Br_2$ mixtures from 850–1140°K. In all these cases, the high temperature rate constants were in good agreement with extrapolations of low temperature data.

Via a flow technique, Reed & Rabinovitch (168) observed the sodium diffusion flame in reactions of Na with fluorinated methyl chlorides at 529°K. Crocco & co-workers (169, 170) have designed a flow reactor for high temperature kinetics and studied the decomposition of ethylene oxide over the range 900–1200°K. Hirschfelder (171) has computed from theory the rate of recombination of atoms on hot surfaces.

Many basic ideas about gas kinetics remain only as plausible assumptions associated with the results of classical techniques. A more fundamental approach is to consider the kinetics of reaction of intersecting molecular beams. For example, Taylor & Datz (172) have studied the interaction of beams of K-atoms and HBr molecules. Green & co-workers (173) propose to velocity

select both the reactant molecular or atomic beams and to study the angular and energy distribution of products to elucidate more clearly the reaction mechanism. From such experiments one will be able to evaluate more critically the concept of "activation energy" for a chemical reaction and to eliminate wall effects. It is also possible to select in addition to translational energy the particular vibrational and rotational state reacting (174). Such studies will be of particular interest in explaining flame and explosion kinetics.

Radiative collisions between molecular and electron beams to produce abnormally excited OH molecules have been studied by Horie & co-workers for $H_2O$, $H_2O_2$, and alcohols (175 to 178).

*Kinetics of gas-solid reactions.*—One may ask several questions about the collision of a gas molecule with a solid surface: (*a*) will it stick?; (*b*) if it bounces, has it changed in energy; how long did it remain close to the surface; and in what direction will it bounce?; and (*c*) if it sticks, will it remain where it struck or, if not, how fast and where will it move? In the attempt to answer these questions, many research papers are published each year. It is convenient to consider first those systems in which the gas over the solid is the vapor liberated by heating the solid, i.e., to consider the kinetics of evaporation and condensation.

*Rates of evaporation and condensation.*—When a molecule "evaporates," it first escapes from a bound position in a crystal lattice to a mobile postion on the surface and then escapes to the vapor phase. The process of crystal growth is essentially the reverse. In the quantitative formulation of the questions posed above, one must define the goemetry and energy levels of the surface, and of the gaseous species; a condensation coefficient, $\alpha$ = the fraction of those molecules striking a surface which stick; a vaporization coefficient, usually assumed equal to the condensation coefficient; and an accommodation coefficient which describes the energy exchange during the collision. The problems of condensation of gases on perfect crystal surfaces were considered many years ago, but experiments did not agree with many of the theoretical predictions. Only in the last few years with the introduction of the theory of imperfect crystals and dislocations has it been possible to formulate an adequate theory of evaporation and crystal growth.

Stranski (179) in an excellent review article on evaporation processes has summarized theoretical and experimental work done on kinetics of evaporation, Horbe, Knacke & Prescher (180) have studied nucleation and condensation phenomena.

One of the most important problems is accurate measurement of $\alpha$. Stern & Gregory (181) have studied the condensation coefficient of iodine vapor on iodine crystals and found $\alpha$ to increase with decreasing temperature. Ramthun & Stranski (182) found no temperature dependence of the condensation coefficient of white phosphorus. Thorn & Winslow (183) have measured vaporization coefficients for the species in equilibrium with graphite at high temperatures. Pound, Simnad & Yang (184) have studied the

condensation of a beam of Ag atoms on various metals and glass. Chandra & Scott (185) have observed the condensation of Ag, Au, and Cu atomic beams on various surfaces. Knacke, Schmolke & Stranski (186) have studied the rate of evaporation and condensation coefficient for various faces of KCl and KI single crystals. Ludemann (187) has explained the tendency of alkali halide vapors to grow twinned crystals. Chomet & Yarwood (188) have studied the condensation and reflection of Ag atoms from various metals.

Hirth & Pound (189) have formulated a theory for evaporation of metal crystals. The role of crystal edges in evaporation has been considered by Sears (190). Sears has also verified the predictions of theory for perfect crystals in his studies of evaporation of *p*-toluidine (191). One of the few quantitative approaches to an understanding of accommodation coefficients is the study of Meyer & Gomer (192) on the interaction of $CH_4$ and $C_2H_6$ with clean graphite surfaces up to 2500°C.

Metal whiskers of Hg, Ti, Zn, Cd, and CdS have been obtained by heating samples in air (193), in low pressures of oxygen (194a, 194b), and in vacuum by vapor deposition (195, 196, 197). Meyer (198) has prepared graphite whiskers. Sears (196) has derived a mechanism of whisker growth based on two-dimensional nucleation on a screw dislocation. Single crystals of transition metal oxides have also been grown in flames (199).

Both the Knudsen and Langmuir vapor pressure techniques, which find much use in high temperature systems, involve measurements of rates of evaporation. A fundamental handicap in each approach is the need to know independently the molecular weight of the vaporizing species. One solution is mass identification with a mass spectrograph, as done by Chupka, Inghram & Berkowitz (200), by Porter & Schoonmaker (201) and by Milne & co-workers (202). Another is via a torque Knudsen apparatus (203, 204). An alternative is that of Kusch & Miller to examine the various velocities in a molecular beam effusing from a Knudsen cell (205, 205a). Still another is by the microbalance weighing method of Margrave (206).

Thorn (207) has analyzed the effusion process from a Knudsen cell and finds 95 per cent of the escaping molecules do so without collision. Since the vapor from the Knudsen cell is the "equilibrium" vapor, this supports the picture of a mobile surface layer on a solid from which the "equilibrium" mixture of species escapes. Interesting geometrical data on evaporation have been obtained with a self-imaging distillation camera (208). Günther (208a) has examined intensity distributions for molecular beams of SiO from various shapes of effusion holes.

Average molecular weight determination in high pressure vapor systems is possible through joint application of transpiration and direct boiling point or static pressure measurements (209, 210). The kinetic problems in transpiration experiments have been quantitatively evaluated by Merten (211) and by Bauer & Zlotnick (212).

*Rates of gas-solid reactions.*—Two types of kinetic studies are common on high temperature reactive gas-solid systems: (*a*) a gross rate of reaction study

on macroscopic samples with the aim of establishing "useful" limits and (*b*) a microscopic study of the detailed mechanism. Studies of the first type were useful, for example, in establishing the fact that the rate of reaction of reinforced plastics with air at 1500–15,000°K. was slow enough to allow their use as a nose cone material (213, 214, 215). Similar work has been done on common metals, alloys, and compounds in the presence of $O_2$, $N_2$, $H_2O$, as presented in Table I (216 to 264). Such studies yield the actual rate of reaction and activation energies (265).

TABLE I

KINETICS OF GAS-METAL REACTIONS

| Element | References | Element | References |
|---|---|---|---|
| (a) Oxidation Studies | | Si | 245, 246 |
| Al | 216, 217 | Ti | 247,248,249 |
| C | 218, 219, 220 | W | 237, 238, 250, 251 |
| Cr | 221, 222 | U | 252 |
| Cu | 223 | Zr | 253, 254, 255, 256 |
| Ge | 224 | (b) Nitridation Studies | |
| Hf | 225 | Al | 258 |
| Fe | 226, 227, 228, 229, 230, 231, 232 | Hf | 257 |
| | | Mg | 258 |
| Pb | 233 | U | 259 |
| Li | 234 | (c) Reaction with Water Vapor | |
| Mg | 235 | C | 260 |
| Mo | 236, 237, 238 | Mg | 261 |
| Ni | 239, 240 | Th | 262 |
| Nb | 241, 242, 243 | W | 263 |
| Pt | 244 | Zr | 264 |

There has been little success in organizing the data obtained, and no one can predict just how a given metal will react. The various theories of oxidation of metals assume diffusion as the rate controlling step, and in some cases the predictions are in excellent agreement with experiment. Unfortunately, the metal surface is always covered with a thin oxide or nitride coating and the nature of the surface is not well known. Several reviews on the detailed mechanisms of oxidation rates have been published (266 to 275).

Recently, there have been very fundamental studies by Gwathmey & coworkers (276) on the kinetics of oxidation of various faces of a single metal crystal and by Law (277) on the kinetics of oxidation of an evaporated Si film.

Reports on the kinetics of oxidation of carbides, nitrides, and sulfides are difficult to interpret because of lack of information about the nature of the reactant surface (278 to 287). One of the most detailed studies on a compound is for $UO_2$ oxidation (288).

The reactions of CO with C (289), $CO_2$ with C (290), $SO_2$ with Ni (291),

S with Fe (292), and $Cl_2$ with Ni (293) have also been studied. Some of these are of special interest since the reaction product is not a protective film but is volatile.

Differential thermal analysis is finding wide application in high temperature kinetic studies (294 to 299).

### Structural Studies of High Temperature Systems

Since the pioneering work of Inghram & Chupka (200) and of Honig (300) in identification of high temperature species with a mass spectrograph, there have been reports of many more unusual gaseous molecules in high temperature systems: $Al_2C_2$, $Ga_2C_2$, $LaC_2$, $Ga_2$, and $Al_2$ (301); $W_3O_9$, $W_4O_{12}$, and $W_5O_{15}$ (302); $MoO_3$, $Mo_4O_{12}$, and $Mo_5O_{15}$ (302a); $V_4O_{10}$ $V_6O_{14}$, $V_6O_{12}$, $V_4O_8$, $V_2O_4$, $VO_2$, and VO (303); LaO (304); BeO, $(BeO)_2$ $(BeO)_3$, $(BeO)_4$, $(BeO)_5$, $(BeO)_6$ and $WO_2$, $WO_3$, and $WO_x \cdot (BeO)_y$ (305); TaO, $TaO_2$ (306); TiO, $TiO_2$ (307); ThO, $ThO_2$ (308); ZrO, $ZrO_2$ (309); $Li_2O$, LiO, and LiONa (310) (all by Chupka, Inghram, Berkowitz & associates); $Ga_2$, $Ga_2O$, $In_2$, $In_2O$, $Cu_2$, $Ag_2$, and $Au_2$ by Drowart & Honig (311, 312, 313); $(NaOH)_2$, $(KOH)_2$, $NaK(OH)_2$, and $FeCl_2$-$Fe_2Cl_4$ by Porter & Schoonmaker (201, 314, 315, 316); $(MX)_n$ by Milne & others (202, 317, 318).

The mass spectrograph offers some possibilities for structural elucidation: fragmentation patterns and appearance potentials, but these are indirect and hard to interpret since fragmentation may involve excited electronic or vibrational states or ion-molecule reactions in the mass spectrograph ionization chamber (319). Drowart & Honig (320) have discussed the use of mass spectroscopic data for determination of molecular dissociation energies. In general, however, one must rely on other techniques for detailed structural data and molecular parameters, and there has been considerable activity in high temperature infrared and microwave spectroscopy, and in high temperature electron diffraction to find out more about bond lengths, bond angles, and vibrational and rotational energy levels in complex high-temperature species.

Although electronic spectra of many high temperature species are known, those for polyatomic molecules are very complex. Spectra of gaseous metal species (Pu, U, etc.) have been observed in carbon tube furnaces (321, 322). Useful structural data have been derived from electronic spectra for the alkali halides (323, 324), for $NH_2$, HCO, and HNO by Ramsay & associates (325, 326, 327); for $CH_3$ by Herzberg & Schoosmith (328); for $C_3$ by Kiess & Broida (329). Typical of a complex, but unanalyzed spectrum is that of $B_2O_3$ obtained by Soulen & Leroi (330), and of a molecule supposed to be $B_2O_2$ obtained by Porter & Dows (331). The ultraviolet spectrum of air from 3000–6000°K. has been reported by Wurster, Glick & associates (332, 333).

A conventional infrared spectrometer is easily modified for high temperature work by separating the source and the entrance slit sufficiently to make room for a high temperature furnace. A variety of complex inorganic gases have been studied at temperatures up to 1800°C.

Klemperer & co-workers have observed fundamental vibrational fre-

quencies for gaseous LiH (334); $AlCl_3$ and $Al_2Cl_6$ (335); $HgCl_2$ and $HgBr_2$ (336); LiCl, LiBr, and LiI (337); NaX, KX, RbCl, and CsCl (337a); $Cu_3Cl_3$ (338); $HgI_2$, $CdCl_2$, $CdBr_2$, $CdI_2$, $ZnCl_2$, $ZnBr_2$, and $ZnI_2$ (339); and $BeF_2$, $BeCl_2$, $Be_2Cl_4$, and $MgCl_2$ (340). For most molecules the low energy bending frequencies were not detected, but this was possible for $BeF_2$, $BeCl_2$, and $MgCl_2$. Klemperer & Berry (341) have used a polarizable ionic model to explain the variations in bending frequencies. From the relative rotational intensities of lines in the *P* and *R* branches of the 0–1 LiH band, Klemperer & Norris (342) have derived a quantity dependent on the dipole moment and its derivative and conclude that an ionic model is not satisfactory for gaseous LiH.

Sidorov & Sobolev (343) have reported an infrared spectrum for gaseous $P_2O_5$. Dows & Porter (344) first observed an infrared emission spectrum of gaseous $B_2O_3$ at 1500–1750°K. and determined the isotope shift on substitution by $B^{10}$ for $B^{11}$. White, Walsh & Mann (345) also have studied this system. Taylor (346) has analyzed the results and eliminated the chemically plausible linear and bipyramidal structures. The data favor either a V-shaped or W-shaped $C_{2v}$ structure or a zigzag $C_2$ structure.

Margrave & Spinar (347) have observed infrared absorptions characteristic of the dimeric gaseous species in equilibrium with alkali hydroxides. Margrave, Greene & Randall (348) have observed characteristic $MgCl_2$, $MgBr_2$, and $NiCl_2$ stretching frequencies, and Greene & Margrave (349) have observed five infrared active frequencies of gaseous $B_2S_3$.

There are many reports of complex high temperature species for which structural data could easily be obtained by this technique: $Al_2O$, AlO (350); $B_2O_2$ (351); $HBO_2$ and $H_3BO_3$ (352, 353); $NaX \cdot ZrX_4$ (354, 355); $NaX \cdot BeF_2$ (356); $MoO_2Cl_2$ (357); $Al_2Br_2Cl_4$ (358); $Zn(OH)_2$ and $WO_2(OH)_2$ (359, 360, 361); $Be(OH)_2$ (362); $NaAlX_4$ (363, 364); as well as the many species identified mass spectrographically.

Vibrational data on high temperature species are also available from Raman spectroscopy. No work on high temperature gases has been reported. Bues (365, 365a) has studied the Raman spectra of fused nitrates and phosphates; Harrand (366) has studied vitreous $SiO_2$ and $B_2O_3$; Sidorov & Sobolev (367) have studied high temperature infrared and Raman absorption of glassy $B_2O_3$.

The high precision molecular parameters available from microwave studies are of great interest for high temperature species. Mechanical problems of construction have, however, limited direct microwave studies to temperatures below 1000°C. All the gaseous alkali halides (except LiF, NaF, KF, RbF, and LiCl) (368, 369), and the OH molecule (370) have been investigated.

A simple microwave apparatus capable of use at high temperatures has been suggested by Costain (371). The absorption cell is simply a pyrex or other extruded tube with a polystyrene lens and microwave horn at each end. Garrison & Gordy (372) have detected microwave absorption by high temperature molecular beams of KCl and NaCl.

Sugden & associates (373 to 376) and Page (377) have studied the attenuation of microwaves in flames to obtain data on the electron affinity of OH and the kinetics and equilibrium constant for the reaction $M+OH \rightleftharpoons MOH$. Evidence has also been reported for $MOH^+$ ions (378).

High temperature electron diffraction has been done almost exclusively in Russia (379). A series of outstanding investigations from the laboratory of Akishin, Spiridonov & co-workers has demonstrated the linearity of a wide variety of triatomic molecules: $ZnX_2$ (380, 381), $CdX_2$ (382), $BeX_2$ (383), $MgX_2$ (384), $CaX_2$ (385), $SrX_2$ (386), and $BaX_2$ (387, 388). $GaX_3$ (389) molecules have been examined recently and a study of $Li_2O$ (390) indicated a slightly bent structure. Data have also been reported for the gaseous beryllium halides (390a). Such data are fundamental in any calculations or predictions about the behavior of metal-halides systems at high temperatures. Tanaka & Hashimoto (391) have designed an electron microscope and diffraction apparatus for use from 700–2000°C.

X-ray diffraction at high temperatures is becoming commonplace and a variety of special cameras and designs are reported (392–401). Typical work is that of Chiotti & co-workers (402) on the high temperature thermal expansion of U. Special apparatus has been developed for high temperature studies of single crystals (403). High temperature neutron diffraction studies of liquid Pb and Bi (404) and of iron have been made (405).

Of special interest, also, are the studies of Zarzycki (406, 407) on the structures of molten fluorides and chlorides which support an ion cluster model. Other information on the "structure" of fused salts is obtained from transport number determinations by Duke & co-workers (408 to 412), Bloom & Doull (413) and others (414), and from other data (415, 416, 417).

## Recent Progress in High Temperature Syntheses

In the broadest sense, chemists are striving to produce useful chemical materials, and high temperatures play an important role in new chemical syntheses for mica (418); for garnet and hornblende (419); for synthetic gems (420); and for other single crystals (421, 422). Preparation of simple fluorocarbons and cracking of hydrocarbons, instead of being accomplished in a routine organic synthesis, many now be done at 2000°C. and higher (423, 424, 425). HCN is prepared directly from methane and ammonia at high temperatures (426). A new high temperature synthesis of acetylene has recently been announced making use of temperatures of 2500°C. (427). The usefulness of titanium depends strongly on the availability of a nonreactive crucible for casting the molten metal (428).

The important possibilities for production of new and unusual materials depend directly on the existence of unusual species which can act as intermediates at high temperatures. Greene & associates (429, 430) have studied the chemical reactions occurring in shock waves through various organic compounds. Rice & Grelecki (431) have prepared the radical $(CH_3)_2N$ at 1300°C. In the C-S system, one finds large quantities of CS(g) at 1400°C. (432, 433); in the C-Cl system, there is a large quantity of $CCl_2$(g) formed in

decomposition of $CCl_4$ (433). A new high temperature synthesis of $CS_2$ from CO and S has been announced (434). Free radicals like these, and of many other types: O, H, OH, N, $NH_2$, CF, $CF_2$, etc., have been the subject of many investigations; almost all are attained via a high temperature, either by direct heating or by an electric discharge. Volatile halides and sub-halides are playing an important role in metal refining by high temperature techniques (435, 436).

With a striking analogy to room temperature solution chemistry there is being developed an extensive high temperature chemistry of systems with water—hydrothermal chemistry. Research in this field is not only important for explaining geologic phenomena, but also is being applied for mineral refining and synthesis of special crystals of high perfection. An extensive review has been prepared by Ellis & Fyfe (437).

Of special interest are the studies of electrical conductivity, ionic dissociation, and solubility of KCl, KOH, and HCl in super critical water by Franck (438, 439, 440); the hydrothermal syntheses of calcite (441); of quartz (442 to 446); of $GeO_2$ (447, 448); of sapphire (449); of zircon, thorite, and huttonite (450); and the pressure-temperature curves for interaction of water with inorganic salts at high temperatures (451 to 454). Wasserburg (455) has suggested the species $Si(OH)_4$ in supercritical quartz-water systems. Livey & Murray (456) have reviewed the high temperature behavior of BeO and MgO in the presence of water vapor. Glemser & associates (359, 360, 361) have reported data on gaseous hydroxides of Zn and W.

Margrave & co-workers (352, 353) have reported the existence of appreciable quantities of gaseous boron hydroxides at temperatures above 1000°C. Such species are the explanation for the "hydrothermal" refining technique for removal of traces of boron from high purity silicon (457).

Synthesis of a new family of crystalline materials made from glass—pyrocerams—was reported by Stookey (458). Homogeneous nucleation of a glass is accomplished by introduction of a small quantity of a sparingly soluble substance to the glass when it is hot. The resulting material is easily formable and yet has high strength, hardness, and thermal shock resistance. A variety of expansion coefficients can be produced.

## Thermodynamic and Physical Properties of High Temperature Materials

One of the most important practical results of research such as that discussed in the previous sections lies in the realm of prediction of high temperature behavior of unstudied systems. As has been frequently pointed out it is not possible to study every imaginable chemical system, and one must seek general trends and rules. Before one can understand a chemical reaction, however, he must know all the species present, their geometry and energy levels, and the way in which they interact. It is the aim of this section to indicate what has been done to assemble information to aid in making predictions about high temperature systems.

*Thermodynamic properties and calculation aids.*—Numerous tables of thermodynamic data have been published. Probably the most useful compilation is that of Stull & Sincke (459) on the properties of the condensed and gaseous elements. Margrave (460) has discussed the use of various functions in high temperature calculations, and also presents a tabulation of free energy functions and heats of formation for gaseous elements to 5000°K. and for condensed binary and ternary oxides, nitrides, sulfides, carbides, and hydroxides up to 2000°K. Kolsky, Gilmer & Gilles (461) have published thermodynamic data for 54 gaseous elements.

Hirschwald, Knacke and Reinitzer (462) have presented an extensive table of high temperature equilibrium data for inorganic compounds, and Horbe & Knacke (463) have summarized 140 vapor pressure curves for metals and their halides, oxides, and sulfides. Tripp & King (464) have discussed thermodynamic properties of oxides at elevated temperatures, and Glassner (465) has revised his table of thermochemical properties of oxides, fluorides, and chlorides up to 2500°K. Kennedy has summarized the pressure-volume-temperature properties of water to 1000°C. and 100 bars pressure (466). Brewer (467) presents values for the dissociation energies of diatomic and triatomic oxides (MO and $MO_2$).

Since interest in rocket propellant systems has stimulated flame temperature and other complex equilibrium calculations, computing techniques have been further developed. Villars (468) has presented a scheme for use of the IBM 701 computer for complex equilibrium calculations.

The calculation of thermodynamic functions for ideal gases and the various approximations usually involved were considered by Brounshtein (469, 470) and Baumann (471). Hiel (472) has discussed the calculation of high temperature transport properties. Thermodynamic and transport properties of air up to 15,000°K. have been considered by Hansen (473), by Moeckel & Weston (474), and by Hilsenrath and Beckett (475). Selivanov and Shlyapintokh (476) have calculated the properties of air from 20,000°K. to 500,000°K. Amdur & associates (477, 478) have developed a theory for calculation of transport properties and virial coefficient for high temperature gases. Mason & Vanderslice (479) have also calculated virial and Joule-Thompson coefficients at extremely high temperatures. The thermal conductivity of a mixture of gases in chemical equilibrium has been calculated for the general case by Butler & Brokaw and shown to agree with experimental data for $N_2O_4 = 2\ NO_2$ and $(HF)_6 = 6\ HF$ (480). High temperature data for the ammonia synthesis equilibrium have been published (481). Calculations on the C-H system at high temperatures are also available (482).

The theoretical behavior of highly ionized gases (plasmas) has been considered by Cowan & Kirkwood (483). Chapman (484) has treated thermal diffusion processes in ionized gases.

Thermodynamic properties at high temperatures have been calculated for gaseous alkali halides (485); $C_2N_2$ and CN (486); Group V hydrides and deuterides (487); for $NO_2$ (488); and for $N_2$ (489).

The quantitative understanding of molten salts is gradually being developed and numerous publications discuss the measurement of equilibrium potentials and chemical reactions in fused LiCl-KCl (490, 491), Ce-$CeCl_3$ (492), cryolite-alumina (493, 494), oxides (495), halides (496), and borates (497). Laitinen (498) has reported high temperature polarography in fused LiCl-KCl mixtures.

Heats of formation, activities, vapor pressures, and other thermodynamic properties have been determined with high precision for cadmium-magnesium (499), cadmium-silver (500), chromium-iron (501), copper-gold (502), copper-gold-silver-nickel (503), lead-tin (504), and silver-gold alloys (505) at various elevated temperatures. A comprehensive bibliography of metallurgical thermodynamic data is being prepared by Hultgren & associates (506).

*Physical properties of high temperature materials.*—Fundamental in all high temperature work are the melting points of the refractory solids. Many cases in the literature indicate differences of 200–500°C. in the reported melting points. New techniques for melting point determinations have been presented (507, 508) and values reported for Pr and Nd (509); for Ge at various pressures (510); for Nb (511); for Ti, Zr, and Hf (512); for $UO_2$ (513, 514); and for ZnS (515). High temperature densities of molten salts were measured by Husband (516).

High temperature dilatometer and length measurements have been discussed by Yamauchi & Suzuki (517), by Szonyi (518), and by White (519). Elliott & Kempter (520) have studied the thermal expansion of transition metal carbides. The high temperature creep of graphite has been studied up to 2000°C. (521).

Surface tensions of molten glasses (522) and of molten iron, cobalt, and nickel (523) have been measured; and the effects of Cr, Sn, In, Ti, Se, and Te additives on the surface tension were investigated (524, 525). Viscosities of $N_2$, $O_2$ and other gases (526, 527) and of liquids (528, 529, 530) were also measured at high temperatures. Thermal conductivity of ceramic materials was considered from the viewpoint of structure and phase distribution (531).

Parker, Pask & associates (532, 533) have shown that ceramic crystals have appreciable ductility and that purity and surface environment play a major role in creating the "normal" ceramic brittleness.

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